

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
22 November 2001 (22.11.2001)

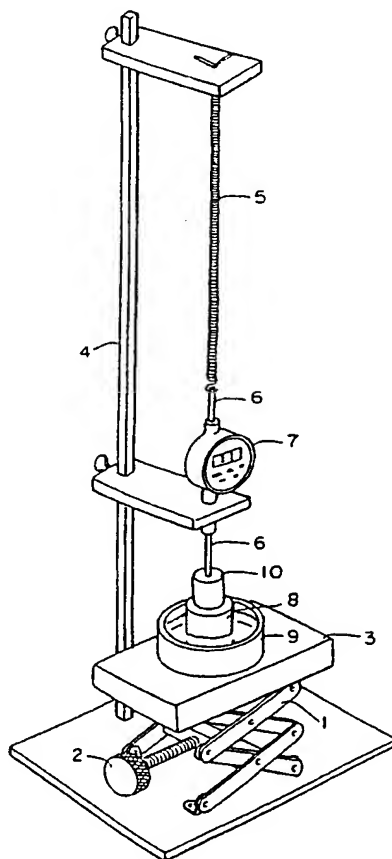
PCT

(10) International Publication Number  
**WO 01/87365 A2**

- (51) International Patent Classification<sup>7</sup>: **A61L 15/00**
- (21) International Application Number: **PCT/US01/12761**
- (22) International Filing Date: **19 April 2001 (19.04.2001)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:  
**09/572,492** **15 May 2000 (15.05.2000)** **US**
- (71) Applicant (for all designated States except US): **KIMBERLY-CLARK WORLDWIDE, INC. [US/US];** 401 North Lake Street, Neenah, WI 54956 (US).
- (72) Inventor: and
- (73) Inventor/Applicant (for US only): **QIN, Jian [US/US];** 1602 East Cranberry Drive, Appleton, WI 54915 (US).
- (74) Agent: **GLANTZ, Douglas;** 5260 Deborah Court, Doylestown, PA 18901-1949 (US).
- (81) Designated States (national): **AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.**
- (84) Designated States (regional): **ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).**

[Continued on next page]

(54) Title: **POLYSACCHARIDE ABSORBENT AND METHOD**



(57) Abstract: Disclosed are novel polysaccharide absorbents and method for providing a water-swellaable, water-insoluble modified polysaccharide having preferred age-stable absorption properties. The novel polysaccharide absorbents and method provide a natural-based absorbent and preferred aging characteristics for absorbency. A natural-based water-soluble carboxyalkylpolysaccharide is dissolved in water and recovered and heat-treated to form a carboxyalkyl polysaccharide which is water swellaable and water insoluble. The water-swellaable and water-insoluble carboxyalkyl polysaccharide having a preferred initial absorbency under load value is aged under at least about 60 percent relative humidity. In one aspect the aqueous mixture of water-soluble carboxyalkyl polysaccharide has a pH between about 4.0 and about 7.5. The natural-based material product having preferred absorbency under load and preferred aging characteristics retains at least about 50 percent of an initial Absorbency Under Load analytical testing value after aging.

10/006781  
WO 01/87365 A2



**Declaration under Rule 4.17:**

— of inventorship (Rule 4.17(iv)) for US only

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**Published:**

— without international search report and to be republished upon receipt of that report

## POLYSACCHARIDE ABSORBENT AND METHOD

### BACKGROUND OF THE INVENTION

#### I. Field of the Invention

The present invention relates to a polysaccharide absorbent and method providing preferred liquid absorbency properties. In one aspect, the present invention relates to a modified polysaccharide and method providing preferred liquid absorbency while under an external pressure and after aging. In one aspect, the present invention relates to a process for the preparation of modified polysaccharides having the preferred liquid absorbency properties.

#### 2. Background

A variety of materials have been described for use as absorbent materials in personal care products. Some natural materials described for use as absorbent materials in personal care products include agar, pectin, gums, carboxyalkyl starch, and carboxyalkyl cellulose. Some synthetic materials described for use as absorbent materials in personal care products include polyacrylates, polyacrylamides, and hydrolyzed polyacrylonitrile. While the natural-based absorbent materials can be used in personal care products, they have not gained widespread usage.

### INTRODUCTION TO THE INVENTION

The natural-based absorbent materials have not gained widespread usage in personal care products at least partly because their absorbent properties are not superior compared to the synthetic absorbent polyacrylate materials.

Many of the natural-based materials form soft, gelatinous masses when swollen with liquid. When used in absorbent products, the soft gelatinous masses cause gel-blocking which prevents liquid transport within a fibrous matrix of the absorbent materials. After gel-blocking occurs, subsequent

insults of liquid cannot be absorbed efficiently by the product, and the product tends to leak.

Further, many of the natural-based materials exhibit poor absorption properties under external pressures.

In contrast, the synthetic absorbent materials are capable of absorbing large quantities of liquid while maintaining a stiff, non-mucilaginous character. The synthetic absorbent materials used in absorbent products today minimize the likelihood of gel-blocking.

Water-swellaable, water-insoluble absorbent materials are used as superabsorbents in disposable absorbent personal care products. The superabsorbents are used in diapers, training pants, adult incontinence products, and feminine care products to increase liquid absorbent capacity. The superabsorbents are provided in absorbent products in a fibrous matrix, such as in a matrix of wood pulp fluff. The absorbent capacity of a matrix of wood pulp fluff alone may be about 6 grams of liquid per gram of fluff. The absorbent capacities of the superabsorbents on the other hand are on the order of at least about 10, preferably at least about 20, and often up to 100 times their weight in water. Incorporating superabsorbents in disposable absorbent personal care products reduces overall bulk while increasing the absorbent capacity.

Carboxyalkyl cellulose materials and other modified polysaccharides are formed from a cellulosic material treated with carboxyalkylating reactants, such as a chloroalkanoic acid, preferably monochloroacetic acid, and an alkali, such as sodium hydroxide, optionally, in the presence of an alcohol. Such a process is described, for example, in Chatterjee et al. U.S. Patent No. 3,723,413. The carboxyalkyl celluloses are water soluble and can be rendered water insoluble.

In Elliott U.S. Patent No. 2,639,239, a water-soluble, alkali metal salt of carboxymethyl cellulose having a degree of substitution of from about 0.5 to about 1 is treated thermally for up to 10 hours to form highly swollen gel particles.



In Chatterjee et al. U.S. Patent No. 3,723,413, a carboxyalkyl cellulose is heat treated in the presence of remaining carboxyalkylating reactants and by-products and becomes water insoluble, providing preferred liquid absorption and retention.

Inklaar U.S. Patent No. 3,345,358 describes preparing a gel-forming derivative of polysaccharides such as carboxymethyl starch. Finely divided carboxymethyl ethers of polysaccharides are acidified by treating with acid in methanol or other water-miscible organic liquid media. Acid carboxymethyl groups are formed on the material. The material is held under acidified, non-hydrolyzing conditions to form ester bonds whereby constituent macromolecules of the material become cross-linked one to another. The material then is neutralized with an alkali. The produced derivatives are described as being capable of forming a gel upon addition to water.

Reid U.S. Patent No. 3,379,720 describes preparing modified polysaccharides, such as ethers and esters of cellulose, including a water-soluble polysaccharide slurry in inert medium, acidifying the polysaccharide, removing excess acid from the acidified polysaccharide, drying, and heat-curing.

Gelman et al. U.S. Patent No. 4,689,408 describes preparing salts of carboxymethyl cellulose. A carboxymethyl cellulose with water is admixed with a non-solvent for the carboxymethyl cellulose, and the carboxymethyl cellulose is recovered. The carboxymethyl cellulose is said to have an absorbency of at least 25 grams of liquid per gram of carboxymethyl cellulose.

The modified polysaccharide materials do not absorb as well as many synthetic highly absorptive materials. The lower absorption level has stood in the way of widespread use of the carboxyalkyl polysaccharides in absorbent personal care products.

There is a need for a natural-based, highly absorbent material having age-stable absorptive properties comparable to

synthetic, highly absorptive materials and suitable for use in personal care absorbent products.

It is an object of the present invention to provide an absorbent and method providing preferred liquid absorbency properties.

It is an object of the present invention to provide a natural-based absorbent and method providing preferred liquid absorbency properties.

It is an object of the present invention to provide a natural-based absorbent and method providing preferred liquid absorbency properties and preferred age stability.

It is another object of the present invention to provide a natural-based absorbent and method providing a modified polysaccharide absorbent and method.

It is still another object of the present invention to provide a natural-based absorbent and method providing a modified polysaccharide absorbent having preferred liquid absorbency while under an external pressure and after aging.

These and other objects of the present invention will become apparent after a review of the detailed description together with the figures of the drawings which follow.

#### SUMMARY OF THE INVENTION

The present invention includes a material and method for providing a natural-based absorbent material having preferred absorbency under load and preferred aging characteristics, including providing a water-soluble carboxyalkyl polysaccharide dissolved in water and recovering and heat-treating the carboxyalkyl polysaccharide to form a carboxyalkyl polysaccharide which is water swellable and water insoluble. The water-swellable and water-insoluble carboxyalkyl polysaccharide having a preferred initial absorbency under load value is aged under at least about 60 percent relative humidity. In one aspect, the aqueous mixture of water-soluble carboxyalkyl polysaccharide has a pH between about 4.0 and about 7.5. The

natural-based material product having preferred absorbency under load and preferred aging characteristics retains at least about 50 percent of an initial Absorbency Under Load analytical testing value after aging.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The sole Figure illustrates the apparatus for determining the Absorbency Under Load values of an absorbent material.

#### DETAILED DESCRIPTION

The present invention provides a water-swellaable, water-insoluble modified polysaccharide having an initially effective absorbency property profile and further having an absorbency property profile which substantially retains preferred liquid absorbency properties after aging.

The material and method of the present invention provide a water-swellaable, water-insoluble carboxyalkyl polysaccharide. The carboxyalkyl polysaccharide is characterized in that it exhibits an effective initial Absorbency Under Load (AUL) value and exhibits an effective stability in its absorbent properties after aging.

In one aspect, the material and method of the present invention provide a carboxyalkyl polysaccharide having an initial Absorbency Under Load value of at least about 14 and which retains at least about 50 percent of its initial Absorbency Under Load value after aging for about 60 days at about 24° C and at least about 30 percent relative humidity.

The present invention further includes methods for producing a water-swellaable, water-insoluble carboxyalkyl polysaccharide that exhibits an effective initial Absorbency Under Load value and exhibits an effective stability in its absorbent properties after aging.

The material and method of the present invention provide a natural-based material having preferred absorbency under load and preferred aging characteristics, including providing

an aqueous mixture of water-soluble carboxyalkyl polysaccharide, wherein the water-soluble carboxyalkyl polysaccharide is dissolved in water; recovering carboxyalkyl polysaccharide from the aqueous mixture to form a recovered carboxyalkyl polysaccharide; heat-treating the recovered carboxyalkyl polysaccharide at a temperature above about 50° C to form a carboxyalkyl polysaccharide which is water swellable and water insoluble, wherein the water-swellable, water-insoluble carboxyalkyl polysaccharide has an initial Absorbency Under Load value of at least 17 and is capable of retaining at least 50 percent of the initial Absorbency Under Load value after being aged under at least about 60 percent relative humidity for 60 days at 24° C.

Preferably, the aqueous mixture of water-soluble carboxyalkyl polysaccharide has a pH between about 4.0 and about 7.5, more preferably a pH between about 6.0 and about 7.5.

The heat treating includes heat-treating the recovered carboxyalkyl polysaccharide at a temperature above about 50° C for a time effective to cross link and form a carboxyalkyl polysaccharide which is water swellable and water insoluble. The aqueous mixture of water-soluble carboxyalkyl polysaccharide preferably includes a homogeneous mixture of water-soluble carboxyalkyl polysaccharide. The carboxyalkyl polysaccharide is prepared from a polysaccharide selected from the group consisting of cellulose, starch, guar, carrageenan, agar, gellan gum, chitin, chitosan, and mixtures of cellulose, starch, guar, carrageenan, agar, gellan gum, chitin, chitosan. In one aspect, the carboxyalkyl polysaccharide is a carboxymethyl polysaccharide. In another aspect, the carboxyalkyl polysaccharide is a carboxymethyl cellulose. In one preferred embodiment, the carboxyalkyl polysaccharide is recovered by evaporative drying. In one preferred embodiment, the water-swellable, water-insoluble carboxyalkyl polysaccharide exhibits an initial Absorbency Under Load value of at least about 20. In one preferred embodiment, the water-swellable, water-

insoluble carboxyalkyl polysaccharide retains at least about 70 percent of the initial Absorbency Under Load value after aging for about 60 days at about 23° C and at least about 60 percent relative humidity. In one preferred embodiment, the water-swellaable, water-insoluble carboxyalkyl polysaccharide retains at least about 50 percent of the initial Absorbency Under Load value after aging for about 60 days at about 23° C and at about 100 percent relative humidity. In one preferred embodiment, the carboxyalkyl polysaccharide is heat-treated at a temperature of from about 100° C to about 200° C for a time of from about 1 minute to about 600 minutes. In another preferred embodiment, the carboxyalkyl polysaccharide is heat-treated at a temperature of from about 100° C to about 200° C for a time of from about 100° C to about 200° C for a time of from about 5 minutes to about 100 minutes.

In another aspect of the present invention as disclosed and claimed in Qin et al. U.S. Patent No. 5,550,189, a mixture is prepared of a water-soluble carboxyalkyl polysaccharide, water, and a cross-linking agent; recovering the carboxyalkyl polysaccharide from the mixture; and heat-treating the recovered carboxyalkyl polysaccharide at a temperature above about 50° C for a time effective to cross-link the carboxyalkyl polysaccharide to render the carboxyalkyl polysaccharide water swellaable and water insoluble, wherein the water-swellaable, water-insoluble carboxyalkyl polysaccharide exhibits an initial Absorbency Under Load value of at least about 14 and retains at least about 50 percent of the initial Absorbency Under Load value after aging for about 60 days at about 24° C and at least about 30 percent relative humidity.

The material and method of the present invention provide a mixture prepared including a water-soluble carboxyalkyl polysaccharide and water. The carboxyalkyl polysaccharide is recovered from the mixture and heat-treated at a temperature for an amount of time effective so that the carboxyalkyl polysaccharide exhibits an effective initial Absorbency Under Load

value and exhibits an effective stability in its absorbent properties after aging.

In one aspect of the present invention as disclosed and claimed in Qin et al. U.S. Patent No. 5,550,189, a mixture is prepared of a water-soluble carboxyalkyl polysaccharide, and water; the carboxyalkyl polysaccharide is recovered from the mixture; and the recovered carboxyalkyl polysaccharide is heat-treated at a temperature between about 200° C and about 250° C for an amount of time between about 50 to about 90 seconds, wherein the heat-treating is effective to cross-link the carboxyalkyl polysaccharide to render the carboxyalkyl polysaccharide water swellable and water insoluble, wherein the water-swellable, water-insoluble carboxyalkyl polysaccharide exhibits an initial Absorbency Under Load value of at least about 14 and retains at least about 50 percent of the initial Absorbency Under Load value after aging for about 60 days at about 24° C and at least about 60 percent relative humidity.

In one aspect of the present invention, a mixture is prepared including a water-soluble carboxyalkyl polysaccharide and water, wherein the mixture has a pH between about 4.0 and about 7.5. The carboxyalkyl polysaccharide is recovered from the mixture and heat-treated at a temperature for an amount of time effective so that the carboxyalkyl polysaccharide exhibits an effective initial Absorbency Under Load value and exhibits an effective stability in its absorbent properties after aging.

One embodiment of the present invention includes a material and method forming a mixture including a water-soluble carboxyalkyl polysaccharide and water, wherein the mixture has a pH between about 4.0 and about 7.5; recovering the carboxyalkyl polysaccharide from the mixture; and heat-treating the recovered carboxyalkyl polysaccharide at a temperature above about 50° C for a time effective to cross-link the carboxyalkyl polysaccharide to render the carboxyalkyl polysaccharide

water swellable and water insoluble, wherein the water-swellable, water-insoluble carboxyalkyl polysaccharide exhibits an initial Absorbency Under Load value of at least about 14 and retains at least about 50 percent of the initial Absorbency Under Load value after aging for about 60 days at about 24° C and at least about 80 percent relative humidity.

Another embodiment of the present invention includes a material and method forming a mixture including a water-soluble carboxyalkyl polysaccharide, citric acid, a catalyst, and water. The carboxyalkyl polysaccharide is recovered from the mixture so that the carboxyalkyl polysaccharide exhibits an effective initial Absorbency Under Load and exhibits an effective stability in its absorbent properties after aging.

One embodiment of the present invention includes a material and method forming a mixture including a water-soluble carboxyalkyl polysaccharide, water, citric acid, and sodium hypophosphite and recovering the carboxyalkyl polysaccharide from the mixture, wherein the water-swellable, water-insoluble carboxyalkyl polysaccharide exhibits an initial Absorbency Under Load value of at least about 14 and retains at least about 50 percent of the initial Absorbency Under Load value after aging for about 60 days at about 24° C and at least about 30 percent relative humidity.

Another embodiment of the present invention includes a material and method forming a mixture including a water-soluble carboxyalkyl polysaccharide, an aluminum ion, and water. The carboxyalkyl polysaccharide is recovered from the mixture so that the carboxyalkyl polysaccharide exhibits an effective initial Absorbency Under Load and exhibits an effective stability in its absorbent properties after aging.

One embodiment of the present invention includes a material and method forming a water-soluble carboxyalkyl polysaccharide, water, and a cross-linking agent including an aluminum ion and recovering the carboxyalkyl polysaccharide from the mixture wherein the water-swellable, water-insoluble

carboxyalkyl polysaccharide exhibits an initial Absorbency Under Load value of at least about 14 and retains at least about 50 percent of the initial Absorbency Under Load value after aging for about 60 days at about 24° C and at least about 30 percent relative humidity.

Another embodiment of the present invention includes a material and method forming a carboxyalkyl polysaccharide in a reaction dispersion, recovering the carboxyalkyl polysaccharide from the reaction dispersion, preparing a mixture including the recovered carboxyalkyl polysaccharide and water, and recovering the carboxyalkyl polysaccharide from the mixture wherein the carboxyalkyl polysaccharide includes an amount of the original crystalline structure of the polysaccharide to be effective so that the carboxyalkyl polysaccharide exhibits an effective initial Absorbency Under Load and exhibits an effective stability in its absorbent properties after aging.

One embodiment of the present invention includes a material product by process and method provided by preparing a reaction dispersion including a solvent and a polysaccharide including an original crystalline structure; adding a carboxyalkylating reagent to the reaction dispersion at conditions effective to allow the carboxyalkylating reagent to react with the polysaccharide to prepare a carboxyalkyl polysaccharide; recovering the carboxyalkyl polysaccharide from the reaction dispersion; preparing a mixture including the recovered carboxyalkyl polysaccharide and water; and recovering the carboxyalkyl polysaccharide from the mixture wherein the carboxyalkyl polysaccharide includes an amount of the original crystalline structure of the polysaccharide to be effective to result in the water-swellaable, water-insoluble carboxyalkyl polysaccharide exhibiting an initial Absorbency Under Load value of at least about 14 and retaining at least about 50 percent of the initial Absorbency Under Load value after aging for about 60 days at about 24° C and at least about 30 percent relative humidity.



Modified polysaccharides in accordance with the material and method of the present invention are water soluble prior to treatment to provide the modified polysaccharide with the preferred initial and age-stable absorbency characteristics.

As used herein, by "water soluble" is meant capable of being dissolved substantially in excess water to form a true solution. A modified polysaccharide will be considered to be water soluble when it dissolves substantially in excess water to form a true solution, thereby losing its initially particulate form and becoming molecularly dispersed throughout the water solution. Alternatively, the modified polysaccharide may swell in water to the extent that it appears to lose its initial structure even though a true solution may not be formed. The water-soluble modified polysaccharides will be free from a substantial degree of cross-linking, as cross-linking tends to render the modified polysaccharides water insoluble.

As used herein, the term "water-swellaable, water-insoluble" is meant to refer to a modified polysaccharide which, when exposed to an excess of a 0.9 weight percent solution of sodium chloride in water, swells to its equilibrium volume but does not dissolve into the solution. A water-swellaable, water-insoluble modified polysaccharide retains its original identity or physical structure during the absorption of the aqueous solution, but in a highly expanded state, and thus must have sufficient physical integrity to resist flow and fusion with neighboring particles. A water-swellaable, water-insoluble modified polysaccharide in accordance with the present invention is one which is effectively cross-linked to be substantially insoluble but still is initially capable of absorbing at least about 14 times its own weight of a 0.9 weight percent solution of sodium chloride in water when under an applied load of about 0.3 pound per square inch.

Modified polysaccharides in accordance with the present invention include the carboxylated, sulfonated, sulfated, and

phosphated derivatives of polysaccharides, their salts, and mixtures of the carboxylated, sulfonated, sulfated, and phosphated derivatives of polysaccharides and their salts.

Examples of polysaccharides in accordance with the present invention include polysaccharides of cellulose, starch, guar, carrageenan, agar, gellan gum, chitin, chitosan, and mixtures thereof.

Carboxyalkyl polysaccharides in accordance with the present invention include carboxyalkyl celluloses of carboxymethyl cellulose, carboxyethyl cellulose, carboxyalkyl starch, carboxyalkyl carrageenan, carboxyalkyl agar, carboxyalkyl gellan gum, and mixtures of carboxymethyl cellulose, carboxyethyl cellulose, carboxyalkyl starch, carboxyalkyl carrageenan, carboxyalkyl agar, carboxyalkyl gellan gum. A preferred carboxyalkyl polysaccharide in accordance with the present invention is carboxyalkyl cellulose, and a preferred carboxyalkyl cellulose in accordance with the present invention is carboxymethyl cellulose.

The polysaccharide material of wood pulp fluff, cotton, cotton linters, starch, and agar may be in the form of fibers or of fibers which have been comminuted to particulate form. The polysaccharide material is dispersed in a solvent, such as water or an alcohol, and carboxyalkylating reagents are added to the dispersion. Carboxyalkylating reagents include a chloroalkanoic acid, such as monochloroacetic acid, and a base, such as sodium hydroxide. The carboxyalkylating reagents are added to the dispersion at conditions effective to allow the carboxyalkylating reagents to react with and modify the polysaccharide. Such effective conditions depend on temperature, pressure, mixing conditions, and relative amounts of materials, solvents and reagents used in the modification of the polysaccharide.

In one aspect, the process of the present invention includes preparing the carboxyalkyl polysaccharide from a polysaccharide including an original crystalline structure and

retaining an effective amount of the original polysaccharide crystallinity wherein such retained crystallinity functions as a cross-linking moiety so that the carboxyalkyl polysaccharide exhibits an effective initial Absorbency Under Load value and exhibits an effective stability in its absorption properties after aging.

In the process of the present invention, the polysaccharide material is dispersed in a solvent and carboxyalkylating reagents are added to the dispersion. The carboxyalkylating reagents are added to the dispersion at conditions effective to allow the carboxyalkylating reagents to react with and modify the polysaccharide while retaining an effective amount of the original crystallinity of the polysaccharide. Such effective conditions depend on temperature, pressure, mixing conditions, and types and relative amounts of materials, solvents and reagents used. The carboxyalkyl polysaccharide then is recovered from the dispersion. The recovered carboxyalkyl polysaccharide then is dispersed in an aqueous mixture and recovered from the mixture. A final recovered crystalline-cross-linked carboxyalkyl polysaccharide includes an amount of the original crystalline structure of the polysaccharide to be effective to result in the crystalline-cross-linked carboxyalkyl polysaccharide exhibiting an effective initial Absorbency Under Load value and exhibiting an effective stability after aging.

Many polysaccharides, such as cellulose and chitin, are highly crystalline materials. The degree of crystallinity depends on the source of the polysaccharide and its processing history. The highly ordered crystalline structures and the less ordered amorphous areas have different reactivities toward incoming chemicals. The difference in reactivities determines that the amorphous areas are substituted first and heaviest, whereas the highly crystalline areas are substituted last and least. Alkali swelling of the polysaccharide improves the accessibility of the modifying reagents into the

crystalline areas and facilitates the modifying reactions. If the overall degree of substitution of the polysaccharide is sufficiently high and the modification relatively uniformly distributed, total solubility of the modified polysaccharide is achieved in an aqueous solution. However, if the overall degree of substitution is relatively low, or the modification relatively unevenly distributed, the resulting modified polysaccharide will have a chain structure of alternating soluble and insoluble segments like a block copolymer. The insoluble segments would be in the crystalline areas remaining after the modification reaction. The crystalline area functions as a cross-linking point for the soluble modified polysaccharide segments. The crystallinity of the initial polysaccharide or of the modified final product is determined analytically by optical microscopy and x-ray diffraction. The modified final product, after dispersion in an aqueous solution, retains some of the fibrous characteristics of the initial polysaccharide.

Carboxymethylation is a modification process which is kinetically controlled and irreversible. When the carboxymethyl substitution has taken place, the arrangement of the carboxymethyl groups along the cellulose chain is fixed. The particular pattern of carboxymethyl substitution on cellulose obtained depends on the reactant ratios and reaction conditions during the synthesis.

In cellulose, the more accessible amorphous regions are substituted preferentially over the crystalline regions. The carboxymethyl groups are not uniformly distributed along the cellulose chain. Excess alkali is used, or the reaction is pushed to a higher degree of substitution, and substitution occurs in the crystalline regions, providing a more uniform pattern of substitution and a more complete water solubility.

A crystalline-cross-linked carboxymethyl cellulose has been found to be capable of being prepared by different processes including using potassium hydroxide as compared to

sodium hydroxide as the alkali in the process; using a less than stoichiometric ratio of alkali to carboxyalkylating reagent, such as chloroacetic acid; using a lower reactant ratio of carboxymethylating reagents to cellulose; varying the solvent composition in the slurry process; or a combination of these different process techniques. Such reaction conditions can promote carboxymethyl cellulose structures which have crystalline cellulose segments as well as carboxyalkylated segments in the final molecular structures. When the carboxymethyl cellulose is dissolved in water, the dispersion remains translucent or fibrous, whereas a soluble, relatively uniformly substituted carboxymethyl cellulose results in a solution that is clear and transparent.

Alkali is used in the preparation of carboxymethyl cellulose as both a swelling agent for the cellulose and a neutralizing chemical for any acids, such as hydrochloric acid, released by the carboxymethylation reaction. Sodium hydroxide is used as the alkali in commercial carboxymethyl cellulose manufacturing processes.

It has been found that the use of potassium hydroxide as the alkali in the carboxymethylation of cellulose produces a more unevenly distributed carboxymethylation pattern, even at a relatively high degree of substitution, than the use of sodium hydroxide. The unevenly distributed carboxymethylation pattern helps preserve part of the native crystallites in the final carboxymethyl polysaccharide product which results in preferred absorbent properties of the carboxymethyl polysaccharide. Conversely, the same process, but with sodium hydroxide in place of potassium hydroxide as the alkali, results in a water-soluble carboxymethyl cellulose with relatively poorer absorbent properties.

The differences between using potassium hydroxide as compared to using sodium hydroxide is believed to be related to the solvation power of the potassium ion. Being a larger cation than the sodium ion, the potassium ion may not be able

to penetrate some of the cellulose crystalline regions, leaving such cellulose crystalline regions intact during ~~carboxymethylation~~ and, thus, resulting in a more unevenly distributed substitution pattern. The unevenly distributed substitution pattern can happen even with relatively highly-substituted carboxymethyl cellulose as, for example, with a degree of substitution greater than 1.

Use of an excess amount of alkali relative to the carboxyalkylating reagent, such as chloroacetic acid, produces a more evenly substituted carboxymethyl cellulose product which is water soluble when the degree of substitution is sufficiently high. However, it has been found that, where there is a deficiency of alkali relative to the carboxyalkylating agent, a water-insoluble and relatively unevenly substituted carboxymethyl cellulose with desirable absorbent properties may be produced. A deficiency in alkali relative to the carboxyalkylating reagent reduces the degree of swelling in the cellulose structure which, in turn, promotes preferential substitution in the amorphous regions as compared to the crystalline regions.

A relatively low ratio of carboxyalkylating reagent to polysaccharide, such as of chloroacetic acid to cellulose, produces a carboxyalkyl polysaccharide with preferred absorbent properties. In addition, a relatively low ratio of carboxyalkylating reagent to polysaccharide provides lower raw material costs and less reaction by-products, both of which are preferred for economic and environmental reasons.

The crystalline-cross-linked carboxyalkyl polysaccharides need to be treated with a homogenization process, by dispersion and recovery from an aqueous mixture, but do not need additional processing steps, such as heat or chemical treatment, to exhibit the preferred initial AUL value and age-stable absorbency properties described in this invention.

Through dispersion of the crystalline-cross-linked carboxyalkyl cellulose in water, the fibrous structure and the

molecular alignment of the modified cellulose chains are reduced. As the soluble segments of the carboxyalkyl cellulose chains start to interpenetrate one another in the dispersion, a random, coil-entangled molecular configuration is created which is subsequently locked in upon drying. Larger aggregates of the crystalline areas might also be formed in the dissolution process which serve as super-junction zones for the carboxyalkyl cellulose chains, allowing a truly three-dimensional network to evolve.

Repeated liquid uptake and removal do not affect the absorbent properties of the crystalline-cross-linked carboxyalkyl cellulose. The stability of the physical cross-links is believed to be dependent on the size of the crystalline areas that serve as the cross-linking junctions. When the crystalline areas are above an effective range, as for example above the micron range, the junctions are stable and will not be susceptible to the attack of water molecules. The effective size of the crystalline areas is reflected in the translucency of the dispersion of the crystalline-cross-linked carboxymethyl cellulose in an aqueous solution. The method recovers the carboxyalkyl polysaccharide from a reaction dispersion without deteriorating the preferred absorption characteristics of the carboxyalkyl polysaccharide of the present invention. The method includes evaporative drying, freeze drying, precipitation, or critical point drying. The modification process may be performed under low moisture conditions. That is, the starting polysaccharide may be wetted with, for example, 1 part of water for each part of starting polysaccharide. Carboxyalkylating reagents then can be mixed with the wetted starting polysaccharide such that carboxyalkylation occurs. Additional water then can be added to the carboxyalkyl polysaccharide to form a mixture of carboxyalkyl polysaccharide and water. In this manner, no recovery step may be necessary between formation of the carboxyalkyl polysaccharide and any further treatment steps, such as the preparation of a

mixture of carboxyalkyl polysaccharide and water, in order to impart the aging stability to the carboxyalkyl polysaccharide. If too much water is present in the starting polysaccharide, however, the carboxyalkylation reaction may not occur to a sufficient degree.

When the carboxyalkyl polysaccharide is a carboxyalkyl cellulose, the carboxyalkyl celluloses suitable for use in the present invention have an average degree of substitution from about 0.3 to about 1.5, from about 0.4 to about 1.2. The degree of substitution refers to the average number of carboxylalkyl groups, such as carboxymethyl groups, present on the anhydroglucose unit of the cellulosic material. The maximum average number of carboxylalkyl groups that may be present on the anhydroglucose unit of the cellulosic material is 3.0. When the carboxyalkyl celluloses have an average degree of substitution within the range of from about 0.3 to about 1.5, the carboxyalkyl celluloses are water soluble prior to treatment of the carboxyalkyl celluloses to provide the carboxyalkyl celluloses with the preferred initial and age-stable absorbency properties of the present invention. Other characteristics, such as the actual pattern of modifying substitution of the polysaccharide, also have an effect on the water-solubility of the carboxyalkyl polysaccharide.

Carboxyalkyl cellulose is available in a wide range of molecular weights. Carboxyalkyl cellulose having a relatively high molecular weight is beneficial for use in the present invention. Nonetheless, a wide range of molecular weights are suitable for use in the present invention. It is most convenient to express the molecular weight of a carboxyalkyl cellulose in terms of its viscosity in a 1.0 weight percent aqueous solution at 25° C. Carboxymethyl celluloses suitable for use in the present invention will have a viscosity in a 1.0 weight percent aqueous solution at 25° C of from about 10 centipoise (10 mPa.s) to about 80,000 centipoise (80,000 mPa.s), preferably from about 500 centipoise (500 mPa.s) to about 80,000



centipoise (80,000 mPa.s), and more preferably from about 1,000 centipoise (1,000 mPa.s) to about 80,000 centipoise (80,000 mPa.s).

The cross-linked carboxyalkyl polysaccharides exhibiting the preferred absorbent properties of the present invention have been found to exhibit relatively low aqueous solution viscosities as compared to carboxyalkyl polysaccharides that do not exhibit the preferred absorbent properties of the present invention. For example, when measured as a 1.0 weight percent amount in a 0.9 weight percent sodium chloride (saline) aqueous solution that has been allowed to reach equilibrium at about 25° C as, for example, after about 18 hours of mixing, the carboxyalkyl polysaccharides of the present invention have been found to exhibit a viscosity of less than about 400 centipoise, preferably less than about 300 centipoise, and more preferably less than about 200 centipoise. The carboxyalkyl polysaccharides of the present invention have been found to exhibit viscosities that are about 50 percent, preferably about 60, and more preferably about 70 percent less than the viscosity exhibited by an otherwise identical carboxyalkyl polysaccharide that has not been prepared or treated to exhibit the preferred absorbent properties of the present invention. For example, if a carboxyalkyl polysaccharide that has not been prepared or treated to exhibit the preferred absorbent properties of the present invention exhibits a viscosity of about 800 centipoise, a carboxyalkyl polysaccharide that has been prepared or treated to exhibit the preferred absorbent properties of the present invention will exhibit a viscosity of less than about 400 centipoise, preferably less than about 320 centipoise, and more preferably less than about 240 centipoise.

The method according to the present invention has been found to produce an improvement in initial AUL values in modified polysaccharides over a wide range of molecular weights. While high molecular weight, modified polysaccha-

rides are preferred, it is important that improvements in low molecular weight, modified polysaccharides can be achieved. Low molecular weight, modified polysaccharides are cheaper than high molecular weight, modified polysaccharides. Accordingly, there is an economic advantage for employing low molecular weight, modified polysaccharides. Further, one can work with aqueous solutions containing relatively high concentrations of low molecular weight, modified polysaccharides compared to aqueous solutions containing high concentrations of high molecular weight, modified polysaccharides. Aqueous solutions of high molecular weight, modified polysaccharides exhibit a high viscosity compared to an aqueous solution containing the same concentration of low molecular weight, modified polysaccharides. For reasons of efficiency, it is preferred to form an aqueous solution including the highest concentration of modified polysaccharides possible while still being able to effectively work with the aqueous solution.

Suitable carboxyalkyl celluloses are commercially available from numerous vendors. Examples of a commercially available carboxyalkyl cellulose is carboxymethyl cellulose, commercially available from the Aqualon Company under the trade designation AQUALON® or BLANOSE® Cellulose Gum.

The carboxyalkyl polysaccharides of the present invention have the ability to absorb a liquid while the carboxyalkyl polysaccharide is under an external pressure or load, herein referred to as Absorbency Under Load (AUL). Synthetic polymeric materials, such as polyacrylates, having a high ability to absorb while under a load, have been found to minimize the occurrence of gel-blocking when incorporated in absorbent products. The method by which the Absorbency Under Load is determined is set forth below in connection with the examples. The Absorbency Under Load values determined as set forth below and reported herein refer to the amount, in grams, of an aqueous solution containing 0.9 weight percent sodium chloride a gram of the modified polysaccharide can absorb in 60 minutes

under a load, for example, of about 0.3 pound per square inch (psi). As a general rule, it is preferred that the carboxy-alkyl polysaccharide has an initial Absorbency Under Load value, for a load of about 0.3 psi, of at least about 14, preferably of at least about 17, more preferably of at least about 20, more preferably of at least about 24, more preferably of at least about 27, and more preferably up to about 50 grams per gram. As used herein, the term "initial Absorbency Under Load" is meant to refer to that AUL value exhibited by a carboxyalkyl polysaccharide as measured within 1 day after preparation of the carboxyalkyl polysaccharide when the carboxyalkyl polysaccharide is stored at ambient conditions, such as at about 24° C and between about 30 to about 60 percent relative humidity. The conditions under which a carboxyalkyl polysaccharide is stored have been found to have an impact on the absorbent properties of the carboxyalkyl polysaccharide as it ages. Even relatively mild conditions, such as ambient conditions, such as about 24° C and at least about 30 percent relative humidity, between about 30 to about 60 percent relative humidity, will result in a degradation of the absorbent properties of the carboxyalkyl polysaccharide as it ages. Storage conditions, such as relatively higher temperatures and relatively higher relative humidities, as compared to ambient conditions, result in quicker and/or more severe degradation of the absorbent properties of the carboxyalkyl polysaccharide as it ages.

Carboxyalkyl polysaccharides of the present invention retain their initial AUL value after aging. Specifically, carboxyalkyl polysaccharides of the present invention retain greater than about 50 percent, and greater than about 70 percent, of their initial AUL value after aging for about 60 days. The aging conditions are at ambient conditions, such as at about 24° C and at least about 30 percent relative humidity. For example, if a carboxyalkyl polysaccharide of the present invention has an initial AUL value of about 20, that

carboxyalkyl polysaccharide may have an AUL value of at least about 10, and of about 14, after aging for about 60 days at about 24° C and at least about 30 percent relative humidity. Otherwise similar carboxyalkyl polysaccharides do not retain the initial AUL value after aging under similar conditions.

The carboxyalkyl polysaccharides of the present invention retain greater than about 50 percent, and more preferably greater than about 70 percent, of their initial AUL value after aging for about 60 days at about 24° C and about 100 percent relative humidity.

As described above, the carboxyalkyl polysaccharide is a carboxyalkyl cellulose, such as carboxymethyl cellulose or carboxyethyl cellulose. The carboxyalkyl cellulose has an initial Absorbency Under Load value of at least about 14, preferably of at least about 17, more preferably of at least about 20, more preferably of at least about 24, and more preferably of at least about 27 and retains greater than about 50 percent, and more preferably greater than about 70 percent of its initial AUL value after aging for about 60 days at about 24° C and at least about 30 percent relative humidity and, more preferably, retains greater than about 50 percent, preferably greater than about 70 percent of its initial AUL value after aging for about 60 days at about 24° C and about 100 percent relative humidity.

The aging phenomenon in respect to the AUL is attributable to the disassociation of cross-linking points of the carboxyalkyl polysaccharide. Cross-linking points can be divided into two groups. First, cross-linking points can be of a relatively permanent cross-linking, such as with ester or amide linkages, resulting, for example, by the use of a polyamine cross-linking agent, or with ionic bonding, resulting, for example, by the use of a polyvalent metal ion cross-linking agent, or with physical cross-links resulting, for example, from a retained crystalline structure. Second, cross-linking points can be of a relatively temporary cross-linking,

such as with hydrogen bonding within the carboxyalkyl polysaccharide. In order to improve the aging stability of the carboxyalkyl polysaccharide, it is preferred to increase the amount of relatively permanent cross-linking that exists within the carboxyalkyl polysaccharide but not to the extent as to over-cross-link the carboxyalkyl polysaccharide.

The carboxyalkyl polysaccharides of the present invention are suitable for use in disposable absorbent garments such as personal care products, such as diapers, training pants, feminine care products, adult incontinent products, and medical products such as wound dressings or surgical capes or drapes.

It has been found that the modified polysaccharides of the present invention may be prepared by certain process steps. An aqueous mixture of a water-soluble carboxyalkyl polysaccharide, water and, optionally, a cross-linking agent, is prepared. The aqueous mixture includes from about 0.01 to about 90 weight percent, preferably from about 0.1 to about 30 weight percent, and more preferably from about 2 to about 25 weight percent based on total mixture weight of the carboxyalkyl polysaccharide. The mixture includes from about 99.99 to about 10 weight percent, preferably from about 99.9 to about 70 weight percent, and more preferably from about 98 to about 75 weight percent water.

The dissolution of the carboxyalkyl polysaccharide into an aqueous mixture is believed to result in entanglement of individual segments of the carboxyalkyl polysaccharide with each other. Such entanglement results in the polysaccharide chains interpenetrating one another in the mixture, so that a random, coil-entangled molecular configuration occurs which is believed to effectively provide cross-linking points and which assists allowing for additional cross-linking of the carboxyalkyl polysaccharide upon further treatment as, for example, with heat-treatment. To allow for effective entanglement of individual segments of the carboxyalkyl polysaccharide with

each other, the mixture is allowed to form a stable, homogeneous mixture at equilibrium prior to additional treatment ~~steps~~ to ensure effective dissolution of the carboxyalkyl polysaccharide into the water. It will be appreciated that a non-water-soluble portion of the carboxyalkyl polysaccharide may exist that will not dissolve into water. For example, the retained crystalline areas of a crystalline-cross-linked polysaccharide will not dissolve in water while the non-crystalline areas will.

The carboxyalkyl polysaccharide is dissolved in a solvent including at least about 30 weight percent water, preferably about 50 weight percent water, more preferably about 75 weight percent water, and more preferably 100 weight percent water. When a co-solvent is employed with the water, other suitable solvents include methanol, ethanol, and acetone. However, the use or presence of such other, non-aqueous solvents may impede the formation of a homogeneous mixture such that the carboxyalkyl polysaccharide chains do not effectively dissolve into the solution and interpenetrate one another.

Cross-linking agents suitable for use in the present invention are water soluble. One suitable cross-linking agent is an organic compound having at least two functional groups or functionalities capable of reacting with the carboxyl, amino, or hydroxyl groups of a carboxyalkyl polysaccharide. It is preferred that the organic cross-linking agent be selected from the group consisting of diamines, polyamines, diols, and polyols and mixtures of diamines, polyamines, diols, and polyols; particularly from the group consisting of primary diols, primary polyols, primary diamines and primary polyamines and mixtures of primary diols, primary polyols, primary diamines and primary polyamines. Of the diols and polyols, those possessing longer carbon chain lengths are preferred. Specifically, the cross-linking agent may be selected from the group consisting of chitosan glutamate, type A gelatin, diethylenetriamine, ethylene glycol, butylene

glycol, polyvinyl alcohol, hyaluronic acid, polyethylene imine and their derivatives and mixtures thereof. Other suitable organic cross-linking agents include monochloroacetic acid, sodium chloroacetate, citric acid, butane tetracarboxylic acid, and amino acids such as aspartic acid, and mixtures thereof.

The presence of a cross-linking agent, particularly a diamine or polyamine, in certain processes of the present invention, may improve the initial Absorbency Under Load value of a carboxyalkyl polysaccharide according to the present invention when compared to an otherwise identical carboxyalkyl polysaccharide without a cross-linking agent in an otherwise similar process. Specifically, the carboxyalkyl polysaccharides prepared using a cross-linking agent may have an initial Absorbency Under Load value of at least about 10 percent, and preferably at least about 20 percent, greater than an otherwise identical carboxyalkyl polysaccharide without a cross-linking agent. The otherwise identical carboxyalkyl polysaccharide will have the same composition and be prepared in a process exactly like the carboxyalkyl polysaccharide of the present invention, except it will not include the cross-linking agent.

Another suitable cross-linking agent includes a metal ion with more than two positive charges, such as  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$ , and  $\text{Ce}^{4+}$ . Suitable metal ion cross-linking agents include those of the transition elements which have vacant d-orbitals. Suitable metal ion cross-linking agents include  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{Ce}_2(\text{SO}_4)_3$ ,  $\text{Zr}(\text{NH}_4)_4(\text{CO}_3)_4$  and  $\text{Ce}(\text{NH}_4)_4(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ , other well known metal ion compounds and mixtures thereof. Such metal ion cross-linking agents, when used with a carboxyalkyl polysaccharide, are believed to form ionic bonds with the carboxyl groups of the carboxyalkyl polysaccharide. Metal ions with only two positive charges, such as  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ , have been found to not provide sufficient cross-linking of the carboxyalkyl polysaccharide to result in the preferred absor-

bent properties of the present invention. The cross-linking agent is used in an amount of from about 0.01 to about 20, preferably of from about 0.05 to about 10, and more preferably of from about 0.1 to about 5 weight percent, based on total weight of the carboxyalkyl polysaccharide present in the mixture.

The order of mixing the carboxyalkyl polysaccharide, water, and cross-linking agent is not critical when a cross-linking agent is used. As such, either the carboxyalkyl polysaccharide or the cross-linking agent may be added to the water and then the remaining material subsequently added, or all three materials may be added together at the same time. However, it may be beneficial, when using certain cross-linking agents, first to add the carboxyalkyl polysaccharide and water and then to add the cross-linking agent to the mixture. For example, if aluminum chloride is used as the cross-linking agent, it may be beneficial that the carboxyalkyl polysaccharide and water first be mixed together and then the aluminum chloride be added to the mixture.

A cross-linking catalyst will not be needed, but may be beneficial, to assist in the cross-linking of the carboxyalkyl polysaccharides of the present invention. For example, if citric acid is used as the cross-linking agent, sodium hypophosphite is preferably used as a cross-linking catalyst. Such cross-linking catalysts can be used in an amount of from about 0.01 to about 3.0 weight percent, more preferably from about 0.1 to about 1.0 weight percent, based on the total weight of the carboxyalkyl polysaccharide used.

The aqueous mixture of a carboxyalkyl polysaccharide, water, and, optionally, a cross-linking agent, can be formed at any temperature at which the carboxyalkyl polysaccharide is soluble in the water. The temperatures will be within the range of from about 10° C to about 100° C. It is preferred to form the mixture with agitation.



The aqueous mixture may be acidic (a pH of less than 7), neutral (a pH of 7), or basic (a pH greater than 7). The mixture can be acidified by the addition of an aqueous solution of an inorganic acid, such as hydrochloric acid or nitric acid, or an aqueous solution of an organic acid, such as acetic acid. Similarly, to provide the aqueous mixture with a basic pH, a base such as an aqueous solution of sodium hydroxide, potassium hydroxide, ammonia, or the like can be added to the mixture.

The aqueous mixture will have a pH within the range of from about 2 to about 12, preferably from about 4 to about 9, more preferably from about 4 to about 7.5, and more preferably from about 6 to about 7.5. The recovered carboxyalkyl polysaccharide will have the same pH as the mixture. However, when the carboxyalkyl polysaccharide is recovered by evaporative drying, the evaporative drying step reduces the pH of the recovered carboxyalkyl polysaccharide if the mixture is initially basic.

When the carboxyalkyl polysaccharide of the present invention is intended for use in personal care products, such as diapers, training pants, and feminine care products, it is preferred that the carboxyalkyl polysaccharide have a neutral character. For this reason, it is preferred that the aqueous mixture be formed with a neutral pH. If the aqueous mixture is formed with an acidic or basic pH, the recovered carboxyalkyl polysaccharide may be acidic or basic (respectively) but may be neutralized. A recovered carboxyalkyl polysaccharide which is acidic in its origin solution may be neutralized, for example, during the recovering process by contacting with a gaseous base such as ammonia. A recovered carboxyalkyl polysaccharide which is basic in its origin solution may be neutralized, for example, during the recovering process by contacting with an acidic gas such as carbon dioxide.

After forming a mixture of carboxyalkyl polysaccharide, water, and, optionally, a cross-linking agent, the carboxy-

alkyl polysaccharide is recovered from the mixture. Any method of recovering the carboxyalkyl polysaccharide from the mixture, without deteriorating the preferred absorption characteristics of the carboxyalkyl polysaccharide, is suitable for use in the present invention. Examples of such methods include evaporative drying, freeze drying, precipitation, critical point drying, and the like.

As used herein, recovery of the carboxyalkyl polysaccharide from the mixture is meant to represent that substantially all of the water is separated from the carboxyalkyl polysaccharide prior to additional treatment steps. Even after removal of substantially all of the water, a small amount of water may remain entrapped within the structure of the carboxyalkyl polysaccharide. The amount of water remaining entrapped within the structure of the carboxyalkyl polysaccharide will depend on the method and conditions under which the carboxyalkyl polysaccharide is recovered. Less than about 15 weight percent, preferably less than about 10 weight percent, and more preferably less than about 5 weight percent, of the original amount of water in the mixture will remain entrapped within the recovered carboxyalkyl polysaccharide.

The carboxyalkyl polysaccharide is recovered from the mixture with evaporative drying. As a general rule, the carboxyalkyl polysaccharide can be recovered by evaporative drying at a temperature within the range of from about 10° C to about 100° C, preferably from about 50° C to about 80° C. Higher temperatures can be employed if the mixture is placed under pressure. Lower temperatures can be employed if the mixture is placed under a vacuum.

Other methods of recovery include precipitation in which a precipitating agent, such as methanol, ethanol or acetone, is added to the mixture of carboxyalkyl polysaccharide, water, and, optionally, a cross-linking agent, to precipitate the carboxyalkyl polysaccharide and the cross-linking agent out of the mixture. The carboxyalkyl polysaccharide then can be

recovered by filtration. If precipitation is used to recover the carboxyalkyl polysaccharide, it may be desirable to wash the recovered carboxyalkyl polysaccharide to remove the precipitating agent.

Depending on the form in which the carboxyalkyl polysaccharide is recovered, it may be necessary or desirable to alter the form of the carboxyalkyl polysaccharide. For example, if evaporative drying is employed, the carboxyalkyl polysaccharide may be recovered in the form of a film or sheet. It may be desirable to comminute the film or sheet material into particles or flakes of material.

The form of the recovered carboxyalkyl polysaccharide preferred will depend to a large extent on the use for which it is intended. When the carboxyalkyl polysaccharide is intended for use in absorbent personal care products, it is preferred that the carboxyalkyl polysaccharide be in the form of a discrete particle, fiber or flake. When in the form of a particle, it is preferred that the particle have a maximum cross-sectional dimension within the range from about 50 micrometers to about 2,000 micrometers, more preferably within the range from about 100 micrometers to about 1,000 micrometers, and most preferably within the range from about 300 micrometers to about 600 micrometers.

The recovered carboxyalkyl polysaccharide may need to be heat-treated at an elevated temperature for a period of time. Such heat-treatment results in cross-linking or additionally cross-linking the carboxyalkyl polysaccharide in order to achieve the preferred initial AUL value and aging stability as described herein.

However, if, for example, citric acid is used as the cross-linking agent and sodium hypophosphite is used as a cross-linking catalyst, it may be possible to prepare a carboxyalkyl polysaccharide which exhibits an effective initial AUL value and preferred aging stability without the need for a further process step, such as heat-treatment, after

recovery of the carboxyalkyl polysaccharide from the aqueous mixture.

\_\_\_\_ If heat-treatment is necessary, any combination of temperature and time effective in achieving a preferred degree of cross-linking, without undesirable damage to the carboxyalkyl polysaccharide, so that the carboxyalkyl polysaccharide exhibits a preferred initial AUL value and aging stability as described herein, is suitable for use in the present invention. When a cross-linking agent is used, the carboxyalkyl polysaccharide will be heat-treated at a temperature within the range from about 50° C to about 250° C, preferably from about 80° C to about 250° C, more preferably from about 100° C to about 200° C, and more preferably from about 100° C to about 160° C. The higher the temperature employed, the shorter the period of time necessary to achieve the preferred degree of cross-linking. It has been found that if very high temperatures are used with an effective length of time, such as a temperature between about 200° C and about 250° C for a length of time between about 50 and about 90 seconds, an effective initial AUL value and sufficient aging stability may be achieved for a carboxyalkyl polysaccharide without the use of a cross-linking agent. The heat-treating process will extend over a time period within the range of from about 1 minute to about 600 minutes, preferably from about 2 minutes to about 200 minutes, and more preferably from about 5 minutes to about 100 minutes.

By providing an aqueous mixture of carboxyalkyl polysaccharide, water, and, optionally, a cross-linking agent, with an acidic character, the time necessary to provide the cross-linking may be shortened. Without intending to be bound hereby, this is believed to be because a weakly acidic carboxyalkyl polysaccharide will have more free carboxylic acid groups present so that more ester linkage bonds may be formed even during a relatively low temperature heat-treatment. Providing the aqueous mixture with a slightly basic

character lengthens the time of the cross-linking process, at a given temperature, compared to a slightly acidic or neutral mixture. Nonetheless, similar general absorptive properties can be achieved with either an acidic, neutral, or basic aqueous mixture. In some instances, it may be preferred to provide the aqueous mixture and the recovered carboxyalkyl polysaccharide with an acidic character in order to lower the temperature or shorten the time of the heat-treatment. In this instance, the carboxyalkyl polysaccharide may be neutralized after the heat-treatment step.

The heat-treating process causes the carboxyalkyl polysaccharide to cross-link or additionally cross-link and become water swellable and water insoluble. Without intending to be bound hereby, it is believed that the heat-treating process causes the carboxyalkyl polysaccharide to undergo a degree of self-cross-linking, not related to the presence of a cross-linking agent, through the formation of ester linkages. This self-cross-linking is in addition to any cross-linking caused by the presence of a cross-linking agent. Further, when the cross-linking agent is a diamine or polyamine, it is believed that cross-linking occurs through amidation of the carboxyl group through the formation of an ammonia salt. Esterification, through a self-cross-linking process, is believed to occur primarily under a weakly acidic, neutral, or slightly basic condition. Esterification, through a self-cross-linking process, is not believed to proceed to a significant degree under relatively basic conditions. Cross-linking attributable to the cross-linking agent may occur under both acidic and basic conditions. Thus, the presence of the cross-linking agent allows for cross-linking to occur over a broad pH range.

A preferred degree or amount of cross-linking of a particular carboxyalkyl polysaccharide provides the initial Absorbency Under Load value and aging stability of the particular modified polysaccharide. If too little cross-linking

occurs, the carboxyalkyl polysaccharide possesses a relatively low initial Absorbency Under Load value because of a lack of gel strength. If too much cross-linking occurs, the carboxyalkyl polysaccharide has a relatively low initial Absorbency Under Load value because of the inability of the carboxyalkyl polysaccharide to absorb liquid.

The presence of cross-links formed by esterification or amidation can be detected through various analytical techniques. Infrared spectroscopy and nuclear magnetic resonance can be used to verify the presence of ester and amide cross-links.

In one aspect, the present invention relates to a water-swallowable, water-insoluble carboxyalkyl polysaccharide characterized in that the carboxyalkyl polysaccharide possesses cross-links formed by esterification and amidation.

In respect to a test method for Absorbency Under Load, the Absorbency Under Load (AUL) test measures the ability of an absorbent material to absorb a liquid (such as a 0.9 weight percent solution of sodium chloride in distilled water) while under an applied load or restraining force.

Referring to the sole Figure, the apparatus and method for determining AUL will be described. Shown is a perspective view of the apparatus in position during a test. Shown is a laboratory jack 1 having an adjustable knob 2 for raising and lowering the platform 3. A laboratory stand 4 supports a spring 5 connected to a modified thickness meter probe 6, which passes through the housing 7 of the meter, which is rigidly supported by the laboratory stand. A plastic sample cup 8, which contains the superabsorbent material sample to be tested, has a liquid-permeable bottom and rests within a Petri dish 9, which contains the saline solution to be absorbed. A weight 10 rests on top of a spacer disc (not visible) resting on top of the superabsorbent material sample (not visible).

The sample cup consists of a plastic cylinder having a 1 inch inside diameter and an outside diameter of 1.25 inches.

The bottom of the sample cup is formed by adhering a 100 mesh metal screen having 150 micron openings to the end of the cylinder by heating the screen above the melting point of the plastic and pressing the plastic cylinder against the hot screen to melt the plastic and bond the screen to the plastic cylinder.

The modified thickness meter used to measure the expansion of the sample while absorbing the saline solution is a Mitutoyo Digimatic Indicator, IDC Series 543, Model 543-180, having a range of 0-0.5 inch and an accuracy of 0.00005 inch (Mitutoyo Corporation, 31-19, Shiba 5-chome, Minato-ku, Tokyo 108, Japan). As supplied from Mitutoyo Corporation, the thickness meter contains a spring attached to the probe within the meter housing. This spring is removed to provide a free-falling probe which has a downward force of about 27 grams. In addition, the cap over the top of the probe, located on the top of the meter housing, is also removed to enable attachment of the probe to the suspension spring 5 (available from McMaster-Carr Supply Co., Chicago, Ill. Item No. 9640K41), which serves to counter or reduce the downward force of the probe to about 1 gram,  $\pm 0.5$  gram. A wire hook can be glued to the top of the probe for attachment to the suspension spring. The bottom tip of the probe is also provided with an extension needle (Mitutoyo Corporation, Part No. 131279) to enable the probe to be inserted into the sample cup.

To carry out the test, a 0.160 gram sample of the absorbent material, which has been sieved to a particle size between 300 and 600 microns, is placed into the sample cup. The sample then is covered with a plastic spacer disc, weighing 4.4 grams, which is slightly smaller than the inside diameter of the sample cup and serves to protect the sample from being disturbed during the test. The 100 gram weight then is placed on top of the spacer disc, thereby applying a load of about 0.3 pound per square inch. The sample cup is placed in the Petri dish on the platform, and the laboratory jack is raised

up until it contacts the tip of the probe. The meter is zeroed. A sufficient amount of saline solution is added to the Petri dish (50-100 milliliters) to begin the test. The distance the weight is raised by the expanding sample as it absorbs the saline solution is measured by the probe. This distance, multiplied by the cross-sectional area inside the sample cup, is a measure of the expansion volume of the sample due to absorption. Factoring in the density of the saline solution and the weight of the sample, the amount of saline solution absorbed is readily calculated. The weight of saline solution absorbed after about 60 minutes is the AUL value expressed as grams saline solution absorbed per gram of absorbent. The readings of the modified thickness meter can be input continuously to a computer (Mitutoyo Digimatic Miniprocessor DP-2 DX) to make the calculations and provide AUL readings. As a cross-check, the AUL also can be determined by the weight difference between the sample cup before and after the test, the weight difference being the amount of solution absorbed by the sample.

#### EXAMPLE I

Two sodium carboxymethyl celluloses (CMC) commercially available from the Aqualon Company under the trade designation AQUALON® Cellulose Gum CMC-7HCF or CMC-9H4F are provided. The CMC-7HCF has an average degree of substitution of about 0.7 and a viscosity in a 1 percent aqueous solution at 25° C of about 1000-2800 centipoise. The CMC-9H4F has an average degree of substitution of about 0.9 and a viscosity in a 1 percent aqueous solution at 25° C of about 2500-6000 centipoise. Each carboxymethyl cellulose is individually dissolved in distilled water to form a solution containing 2 weight percent carboxymethyl cellulose based on total solution weight. A cross-linking agent is dissolved in water to form a solution containing 0.5 weight percent of the cross-linking agent based on total solution weight. The cross-linking



agents employed are chitosan glutamate, commercially available from Protan Biopolymer A/S, Norway, under the trade designation Sea Cure G; 1,4-butylene glycol, commercially available from the Aldrich Chemical Company; polyethylene imine (molecular weight 50,000-100,000) commercially available from Polysciences, Inc.; sodium salt of hyaluronic acid commercially available from Sigma; Type A gelatin commercially available from the Aldrich Chemical Company under the trade designation 300 Bloom; and diethylene triamine commercially available from the Aldrich Chemical Company. The aqueous solution containing the cross-linking agent is then added to the individual aqueous solutions containing the carboxymethyl cellulose to provide various concentrations of cross-linking agent based on total weight of the carboxymethyl cellulose present in the aqueous solution. The resulting mixtures containing water, carboxymethyl cellulose, and cross-linking agent are then thoroughly mixed. The carboxymethyl cellulose is recovered from the solution by evaporative drying at 80° C in a Blue M air-convection oven. After drying, the recovered carboxymethyl cellulose is ground into granules in a blender and heat-treated at various times and temperatures in an oven. Various combinations of carboxymethyl cellulose, cross-linking agent, concentration of cross-linking agent, heat-treatment temperature and heat-treatment time are made. The initial Absorbency Under Load values of the various carboxymethyl celluloses so prepared are measured. The exact combination of carboxymethyl cellulose and cross-linking agent and its initial AUL value are set forth in Table 1. Similarly, control samples of the carboxymethyl cellulose CMC-7HCF and CMC-9H4F are tested for AUL values. These results are also set forth in Table 1.

TABLE 1

Sample No.	CMC	Crosslinking Agent	Crosslinking Agent Concentration <sup>1</sup>	Treatment Temp. (°C)	Treatment Time (min)	Initial AUL Value (g/g)
1	CMC-7HCF	None	--	--	--	4.9
2	CMC-7HCF	None	--	150	35	22.3
3	CMC-7HCF	Chitosan Glutamate	0.3	--	--	7.1
4	CMC-7HCF	Chitosan Glutamate	0.3	140	60	22.6
5	CMC-7HCF	Chitosan Glutamate	0.3	140	70	29.2
6	CMC-7HCF	Chitosan Glutamate	0.3	140	75	31.8
7	CMC-7HCF	Chitosan Glutamate	0.3	140	90	22.9
8	CMC-7HCF	Chitosan Glutamate	0.5	--	--	4.8
9	CMC-7HCF	Chitosan Glutamate	0.5	125	60	13.2
10	CMC-7HCF	Chitosan Glutamate	0.5	140	20	14.4
11	CMC-7HCF	Chitosan Glutamate	0.5	140	30	22.2
12	CMC-7HCF	Chitosan Glutamate	0.5	140	35	24.3
13	CMC-7HCF	Chitosan Glutamate	0.5	140	40	21.9
14	CMC-7HCF	Chitosan Glutamate	1.0	--	--	6.0
15	CMC-7HCF	Chitosan Glutamate	1.0	125	60	15.6
16	CMC-7HCF	Chitosan Glutamate	1.0	125	90	17.6
17	CMC-7HCF	Chitosan Glutamate	1.0	125	110	19.8
18	CMC-7HCF	Chitosan Glutamate	1.0	125	120	18.4
19	CMC-9H4F	None	--	--	--	6.5
20	CMC-9H4F	Chitosan Glutamate	0.5	--	--	7.1
21	CMC-9H4F	Chitosan Glutamate	0.5	130	80	22.4
22	CMC-9H4F	Chitosan Glutamate	0.5	130	90	27.1
23	CMC-9H4F	Chitosan Glutamate	0.5	140	30	24.4
24	CMC-9H4F	Chitosan Glutamate	0.5	150	30	21.7

<sup>1</sup> Weight percent based on total weight carboxymethyl cellulose

TABLE 1 (Continued)

Sample No.	CMC	Crosslinking Agent	Crosslinking Concentration <sup>1</sup>	Treatment Temp. (°C)	Treatment Time (min)	Initial AUL Value (g/g)
25	CMC-7HCF	1,4-butylene glycol	0.5	150	40	19.7
26	CMC-7HCF	1,4-butylene glycol	0.5	150	50	25.5
27	CMC-7HCF	1,4-butylene glycol	0.5	150	60	25.8
28	CMC-7HCF	1,4-butylene glycol	0.5	150	80	22.9
29	CMC-7HCF	1,4-butylene glycol	1.0	150	30	22.2
30	CMC-7HCF	1,4-butylene glycol	1.0	150	50	25.5
31	CMC-7HCF	1,4-butylene glycol	1.0	150	70	25.8
32	CMC-7HCF	1,4-butylene glycol	1.0	150	80	22.9
33	CMC-7HCF	polyethylene imine	1.0	150	10	13.2
34	CMC-7HCF	polyethylene imine	1.0	150	20	17.3
35	CMC-7HCF	polyethylene imine	1.0	150	30	15.7
36	CMC-7HCF	polyethylene imine	2.0	150	20	17.3
37	CMC-7HCF	polyethylene imine	2.0	150	30	21.5
38	CMC-7HCF	polyethylene imine	2.0	150	50	15.7
39	CMC-7HCF	hyaluronic acid	0.5	---	--	6.3
40	CMC-7HCF	hyaluronic acid	0.5	150	30	23.0
41	CMC-7HCF	hyaluronic acid	0.5	150	40	27.9
42	CMC-7HCF	hyaluronic acid	0.5	150	45	28.3
43	CMC-7HCF	hyaluronic acid	0.5	150	50	27.9
44	CMC-7HCF	gelatin	2.0	125	40	16.3
45	CMC-7HCF	gelatin	2.0	125	50	19.7
46	CMC-7HCF	gelatin	2.0	125	60	17.8
47	CMC-7HCF	diethylene triamine	2.0	125	60	8.6
48	CMC-7HCF	diethylene triamine	2.0	125	105	17.2

<sup>1</sup> Weight percent based on total weight carboxymethyl cellulose

In reference to Table 1, the method according to the present invention significantly increases the initial Absorbency Under Load value of the starting carboxymethyl cellulose materials. All of the cross-linking agents employed are effective to increase the initial Absorbency Under Load values. Further, it is seen that the cross-linking agents are effective over a range of concentrations.

#### EXAMPLE II

The chitosan glutamate aqueous solution employed in Example I is weakly acidic. In order to evaluate the effect of pH, a basic cross-linker (diethylenetriamine, commercially available from the Aldrich Chemical Company), is used. Again, a carboxymethyl cellulose (CMC-7HCF) is dissolved in distilled water to form a 2 weight percent aqueous solution. The diethylenetriamine is dissolved in water to form a 0.5 weight percent aqueous solution. The aqueous solution of diethylenetriamine is then added to the aqueous solution of carboxymethyl cellulose to provide a diethylenetriamine concentration of 2.0 weight percent based on total weight of the carboxymethyl cellulose present in the aqueous solution. The carboxymethyl cellulose is then recovered by evaporative drying and comminuted into particles as described in Example I. A comparison material is prepared by dissolving carboxymethyl cellulose (CMC-7HCF) in distilled water to form a 2 weight percent solution. To the aqueous solution of carboxymethyl cellulose is then added 0.004 weight percent sodium hydroxide. The comparison carboxymethyl cellulose is recovered and comminuted into particles as described in Example I. Both samples are then heated at various temperatures for 30 minutes. The resulting polymers are tested for initial Absorbency Under Load. The results of the testing are set forth in Table 2.

TABLE 2

Sample No.	Composition	Treatment Temp (°C)	Treatment Time (min.)	AUL Value (g/g)
49	CMC/diethylenetriamine	80	30	6.2
50	CMC/diethylenetriamine	110	30	6.2
51	CMC/diethylenetriamine	120	30	6.5
52	CMC/diethylenetriamine	130	30	7.7
53	CMC/diethylenetriamine	140	30	13.1
54	CMC/diethylenetriamine	150	30	17.9
55	CMC/diethylenetriamine	160	30	15.9
56	CMC/diethylenetriamine	170	30	14.0
57	CMC/sodium hydroxide	80	30	6.1
58	CMC/sodium hydroxide	110	30	6.0
59	CMC/sodium hydroxide	120	30	5.6
60	CMC/sodium hydroxide	130	30	6.0
61	CMC/sodium hydroxide	140	30	5.9
62	CMC/sodium hydroxide	150	30	5.3
63	CMC/sodium hydroxide	160	30	5.4
64	CMC/sodium hydroxide	180	30	4.3

In reference to Table 2, the carboxymethyl cellulose without a cross-linking agent, under basic conditions, exhibits its no improvement in initial Absorbency Under Load values through the heat-treating step. In contrast, the carboxymethyl cellulose containing the basic cross-linker, diethylene triamine, is seen to exhibit an improvement in initial AUL value as a result of the heat-treating step. This is believed to indicate that a self-cross-linking of the carboxymethyl cellulose does not readily occur at relatively basic pH.

### EXAMPLE III

Sample Nos. 65-71 are prepared by forming an aqueous solution containing 2 weight percent of carboxymethyl cellulose (CMC-7HCF). To the aqueous solution is added an amount of sodium hydroxide sufficient to bring the pH of the solution to 9. No cross-linking agent is present in the solution. The carboxymethyl cellulose is then, according to the method of Example I, recovered, comminuted, heat-treated at 150° C for various times, and tested for Absorbency Under Load.

Sample Nos. 72-77 are prepared by forming an aqueous solution including 2 weight percent carboxymethyl cellulose (CMC-7HCF). To the solution is then added 0.5 weight percent chitosan glutamate in the manner set forth in Example I. The solution is found to have a pH of about 7.4. The carboxymethyl cellulose is then, according to the method of Example I, recovered, comminuted, heat-treated at 150° C for various times and tested for initial Absorbency Under Load.

Sample Nos. 78-103 are prepared in the same manner as Sample Nos. 72-77, except sodium hydroxide is added to the aqueous solution containing carboxymethyl cellulose and chitosan glutamate prior to recovery. The amount of sodium hydroxide added is sufficient to bring the pH of the solution to 9.2, 10.1, or 10.9. The carboxymethyl cellulose is then, according to the method of Example I, recovered, comminuted,

heat-treated at 150° C for various times and tested for initial Absorbency Under Load.

The results of this testing (sample nos. 65-103) are set forth in Table 3.

In reference to Table 3, basic carboxymethyl cellulose containing no cross-linking agent (Sample Nos. 65-71) exhibits no significant improvement in initial Absorbency Under Load values as a result of heat-treatment. In contrast, Sample Nos. 72-103 show improvements in initial AUL values. It is seen that, at a lower pH, the heat-treatment time required to optimize initial AUL values is shorter than at a higher pH.

#### EXAMPLE IV

A carboxymethyl cellulose commercially available from Aqualon Company under the trade designation AQUALON™ Cellulose Gum CMC-7L is provided. This carboxymethyl cellulose has a relatively low molecular weight exhibiting a viscosity in a 2 percent aqueous solution at 25° C of about 25-50 centipoise. Sample No. 104 (comparative) is prepared by forming an aqueous solution containing 2 weight percent of the carboxymethyl cellulose (CMC-7L). The carboxymethyl cellulose is recovered and dried as described in Example I. The material is found to have an initial Absorbency Under Load value of 2.1. Sample No. 105 (comparative) is prepared in the same manner as Sample No. 104 with the exception that, after recovery, the material is comminuted and heat-treated at 170° C for 160 minutes. The resultant material is found to have an initial Absorbency Under Load value of 8.6. Neither material contains a cross-linking agent.

Sample No. 106 is prepared by forming an aqueous solution containing 2 weight percent of the carboxymethyl cellulose (CMC-7L). To the aqueous solution is added 1 weight percent chitosan glutamate in the manner set forth in Example I. The carboxymethyl cellulose is then recovered and comminuted as

TABLE 3

Sample No.	Crosslinking Agent	pH	Treatment Temp (°C)	Treatment Time (min)	Initial AUL Value (g/g)
65	None	9.0	--	--	4.9
66	None	9.0	150	30	6.9
67	None	9.0	150	50	6.9
68	None	9.0	150	80	6.6
69	None	9.0	150	110	6.5
70	None	9.0	150	150	6.6
71	None	9.0	150	180	6.4
72	Chitosan glutamate	7.4	--	--	4.8
73	Chitosan glutamate	7.4	150	15	11.1
74	Chitosan glutamate	7.4	150	22	19.6
75	Chitosan glutamate	7.4	150	30	22.4
76	Chitosan glutamate	7.4	150	45	20.2
77	Chitosan glutamate	7.4	150	60	17.8
78	Chitosan glutamate	9.2	--	--	4.9
79	Chitosan glutamate	9.2	150	15	7.3
80	Chitosan glutamate	9.2	150	30	10.6
81	Chitosan glutamate	9.2	150	45	19.5
82	Chitosan glutamate	9.2	150	60	23.5
83	Chitosan glutamate	9.2	150	70	24.1
84	Chitosan glutamate	9.2	150	80	23.2
85	Chitosan glutamate	9.2	150	120	25.0
86	Chitosan glutamate	9.2	150	150	26.5
87	Chitosan glutamate	9.2	150	180	27.4
88	Chitosan glutamate	9.2	150	240	21.6
89	Chitosan glutamate	10.1	--	--	4.9
90	Chitosan glutamate	10.1	150	30	7.1
91	Chitosan glutamate	10.1	150	60	8.3
92	Chitosan glutamate	10.1	150	120	16.1
93	Chitosan glutamate	10.1	150	150	19.3
94	Chitosan glutamate	10.1	150	180	21.3
95	Chitosan glutamate	10.1	150	210	20.5
96	Chitosan glutamate	10.1	150	240	23.0
97	Chitosan glutamate	10.9	--	--	4.9
98	Chitosan glutamate	10.9	150	60	7.2
99	Chitosan glutamate	10.9	150	110	9.6
100	Chitosan glutamate	10.9	150	120	12.3
101	Chitosan glutamate	10.9	150	150	13.8
102	Chitosan glutamate	10.9	150	180	15.8
103	Chitosan glutamate	10.9	150	240	19.4



set forth in Example I. The resultant material is then heat-treated at 170° C for two hours. The resulting material is found to have an initial Absorbency Under Load value of about 14.7.

From the above, it is seen that the presence of the chitosan glutamate cross-linking agent greatly improves the initial Absorbency Under Load value of low molecular weight carboxymethyl cellulose compared to non-heat-treated materials and heat-treated materials not containing a cross-linking agent.

#### EXAMPLE V

To determine the aging characteristics of absorbent material according to the present invention and comparative absorbent material, the following samples are provided:

Sample No. 107 is prepared similarly to Sample No. 2.

Sample No. 108 is prepared similarly to Sample Nos. 25-28, except the material is heated at 150° C for 70 minutes.

Sample No. 109 is prepared similarly to Sample No. 42. A different initial AUL value is obtained.

Sample No. 110 is prepared similarly to Sample No. 24, except the material is heated for 20 minutes.

Sample No. 111 is prepared according to the method of Example I employing ethylene glycol as the cross-linking agent. The material is heat-treated at 170° C for 30 minutes.

Sample Nos. 107-111 were placed in a temperature and humidity controlled environment. The temperature was maintained at 24° C and the humidity was maintained at 30 percent relative humidity. The samples were tested for AUL value at various points throughout the 60-day aging study. The results are set forth in Table 4. The reported "AUL retention" is the 60-day AUL reported as a percentage of day 0 (initial) AUL. That is, 60-day AUL divided by 0 day AUL.

In reference to Table 4, while heat-treatment alone can, in the absence of a cross-linking agent, provide an acceptable initial AUL, the 60-day AUL retention is only 34.5 percent (Sample No. 107). The presence of a cross-linking agent according to the present invention provides an preferred 60-day AUL retention (Sample Nos. 108-111).

#### EXAMPLE VI

The use of polyvalent metal ions is evaluated for use as cross-linking agents. A carboxymethyl cellulose is dissolved in distilled water to form solutions containing 2 weight percent carboxymethyl cellulose based on total solution weight. A metal ion cross-linking agent is dissolved in water to form a solution. The aqueous solution containing the metal ion cross-linking agent is then added to individual aqueous solutions containing the carboxymethyl cellulose to provide various concentrations of cross-linking agent based on total weight of the carboxymethyl cellulose present in the aqueous solution. The resulting mixtures containing water, carboxymethyl cellulose, and cross-linking agent are then thoroughly mixed. The carboxymethyl cellulose is recovered from the solution by evaporative drying at between about 30° C and about 50° C. After drying, the recovered carboxymethyl cellulose is ground and screened into 300 to 600 micrometer granules. The granules are then heat-treated at various times and temperatures in an oven. Various combinations of carboxymethyl cellulose, metal ion cross-linking agent, concentration of cross-linking agent, heat-treatment temperature and heat-treatment time are made. The initial Absorbency Under Load values, as well as the aging characteristics, of the various carboxymethyl celluloses so prepared are measured. For the aging characteristics testing, ambient conditions of about 23° C and between about 30 to about 60 percent relative humidity are used. The exact combination of carboxymethyl cellulose and cross-linking agent and

TABLE 4  
AUL Value (g/g)

Sample No.	0 days	4 days	8 days	12 days	26 days	50 days	60 days	AUL Retention
107	22.3	17.0	14.2	17.7	12.1	7.6	7.7	34.5
108	25.9	20.9	22.5	22.4	20.9	20.9	21.5	83.1
109	24.5	22.7	21.8	21.8	19.3	18.1	18.8	76.7
110	21.8	20.4	20.9	19.7	17.0	15.1	16.2	74.3
111	21.5	20.1	17.9	18.5	16.3	16.1	15.8	73.5

its AUL value are set forth in Table 5. Similarly, control samples of the carboxymethyl cellulose are tested for AUL values. These results are also set forth in Table 5.

Sample No. 126 is prepared similarly to Sample No. 114 and placed in a temperature and humidity controlled environment. The temperature is maintained at about 23° C and the humidity is maintained at about 100 percent relative humidity. The samples are tested for AUL value at various points throughout an aging study. The results are set forth in Table 6.

Carboxymethyl cellulose (Aqualon CMC-7H4F) is dissolved in distilled water to give 2 weight percent solutions and mixed using a commercial Hobart mixer run at low to medium speed. Various amounts of ammonium zirconium carbonate (AZC) is added to the solutions. The solutions are dried at 50° C overnight in a convection oven. After grinding and sieving, the samples are tested for AUL values wherein the post heat-treatment time is 0 minutes. A post heat-treatment (curing), at a temperature of 110° C for various lengths of time, is used to additionally cross-link the samples. The samples are again tested for AUL values. The results are set forth in Table 7.

Carboxymethyl cellulose (Aqualon CMC-7H4F) is dissolved in distilled water to give 2 weight percent solutions and mixed using a commercial Hobart mixer run at low to medium speed. For Samples 133-141, 3 weight percent ammonium zirconium carbonate, based on the weight of carboxymethyl cellulose, is added to the solutions. For Sample 142, 1 weight percent ammonium zirconium carbonate, based on the weight of carboxymethyl cellulose, is added to the solution. Sample 133 is dried at 50° C for two days in a convection oven. Samples 134-135 are dried at 50° C for four days in a convection oven. Samples 136-141 are dried at 80° C for four days in a convection oven. Sample 142 is dried at 80° C for two days in a convection oven and then post heat-treated for 20 minutes at

TABLE 5

Sample No.	CMC	Crosslinking Agent	Crosslinking Agent Concentration <sup>1</sup>	Treatment Temp. (°C)	Treatment Time (min)	AUL Value (g/g)	
						0 days	200 days
112	CMC-7H4F	--	--	--	--	7.1	--
113	CMC-7H4F	--	--	140	90	22.7	10.4
114	CMC-7H4F	AlCl <sub>3</sub>	0.5	--	--	19.0	19.2
115	CMC-7H4F	AlCl <sub>3</sub>	0.5	110	90	24.1	20.4
116	CMC-7H4F	FeCl <sub>3</sub>	0.6	--	--	8.7	--
117	CMC-7H4F	FeCl <sub>3</sub>	0.6	115	25	22.4	14.7
118	CMC-7H4F	Ce(NH <sub>4</sub> ) <sub>4</sub> (SO <sub>4</sub> ) <sub>4</sub> · 2H <sub>2</sub> O	1.78	--	--	8.7	--
119	CMC-7H4F	Ce(NH <sub>4</sub> ) <sub>4</sub> (SO <sub>4</sub> ) <sub>4</sub> · 2H <sub>2</sub> O	1.78	115	25	21.3	15.8
120	CMC-7H4F	ZnCl <sub>2</sub>	0.77	--	--	7.0	--
121	CMC-7H4F	ZnCl <sub>2</sub>	0.77	130	120	23.5	10.3
122	CMC-7H4F	CaCl <sub>2</sub>	0.63	--	--	7.5	--
123	CMC-7H4F	CaCl <sub>2</sub>	0.63	130	120	23.5	8.5
124	CMC-7H4F	MgCl <sub>2</sub>	0.53	--	--	7.6	--
125	CMC-7H4F	MgCl <sub>2</sub>	0.53	130	120	23.3	8.2

<sup>1</sup> Weight percent based on total weight carboxymethyl cellulose

TABLE 6

Sample No.	AUL Value (g/g)			
	0 days	10 days	20 days	30 days
126	19.0	15.6	16.6	16.4
				15.3

80° C After grinding and sieving, the samples are placed in a temperature and humidity controlled environment. The temperature is maintained at about 23° C and the humidity is maintained at about 100 percent relative humidity. The samples are tested for AUL values at various points throughout an aging study. The results are set forth in Table 8.

Carboxymethyl cellulose [prepared from a cellulose pulp prepared using a Kraft process from a northern hardwood, wherein sodium hydroxide is used in a caustic treatment after bleaching; and wherein the cellulose pulp exhibits a viscosity of about 43 centipoise and a degree of polymerization (number average) of about 2023; and wherein the carboxymethyl cellulose has a degree of substitution in the range of from about 0.7 to about 0.9] is dissolved in distilled water to give 2 weight percent solutions and mixed using a commercial Hobart mixer run at low to medium speed. Ferric chloride (0.6 weight percent, based on weight of the CMC) is added to the solutions. The solutions are dried at 80° C overnight in a convection oven. After grinding and sieving, the samples are tested for AUL values. A post heat-treatment, at a temperature of 140° C for various lengths of time, is used to additionally cross-link the samples. The samples are again tested for AUL values. The results are set forth in Table 9.

Sample No. 144 represents the material from Table 9 wherein the CMC is post heat-treated at a temperature of 140° C for 25 minutes. Sample No. 145 represents the material from Table 9 wherein the CMC is post heat-treated at a temperature of 140° C for 30 minutes. These samples are placed in a temperature and humidity controlled environment. The temperature is maintained at about 23° C and the humidity is maintained at about 100 percent relative humidity. The samples are tested for AUL value at various points throughout a 20-day aging study. The results are set forth in Table 10.

TABLE 7

Sample No.	AZC/CHC Wt. ratio	Curing Time (mins)											
		0	10	20	30	40	50	60	80	100	160	200	
127	0/100	6.5	--	--	6.7	--	--	6.5	--	6.6	--	6.9	
128	0.5/100	9.5	--	--	--	--	--	--	--	--	--	--	
129	1/100	13.0	--	--	--	--	--	--	--	--	--	--	
130	2/100	20.5	20.1	20.6	20.8	20.6	--	20.8	21.0	21.2	19.2	17.5	
131	3/100	23.0	--	21.6	24.1	--	21.4	--	19.0	--	17.6	--	
132	4/100	21.4	--	18.1	18.7	--	17.3	--	16.3	--	13.6	--	

TABLE 8

AUL Value (g/g)

Sample	0 days	9 days	10 days	11 days	13 days	20 days	22 days
133	19.9	--	--	16.7	--	17.6	--
134	20.8	--	--	--	18.2	--	19.9
135	15.6	--	--	--	17.7	--	18.5
136	21.0	--	20.3	--	--	19.9	--
137	20.8	--	19.8	--	--	19.7	--
138	21.4	--	--	--	18.5	--	16.8
139	19.7	--	--	--	18.1	--	19.3
140	18.4	--	--	--	18.4	--	19.1
141	18.4	--	--	--	18.3	--	19.4
142	20.1	16.8	--	--	--	17.1	--

Carboxymethyl cellulose is dissolved in distilled water to give 2 weight percent solutions and mixed using a commercial Hobart mixer run at low to medium speed. Samples 146 and 148 use Aqualon CMC-7H4F for the carboxymethyl cellulose. Sample 147 uses a carboxymethyl cellulose similar to the carboxymethyl cellulose prepared for further treatment to prepare the sample used in Table 9. Various amounts of trivalent cerium sulfate salt is added to the solutions. The solutions are dried at 80° C overnight in a convection oven. After grinding and sieving, the samples are tested for AUL values. A post heat-treatment, at a temperature of 140° C for various lengths of time, is used to additionally cross-link the samples. The samples are again tested for AUL values. The results are set forth in Table 11.

Sample No. 149 represents the material from Table 11 with a CMC/Ce<sub>2</sub> (SO<sub>4</sub>)<sub>3</sub> weight ratio of 100 to 1 wherein the CMC is post heat-treated at a temperature of 140° C for 60 minutes. This sample is placed in a controlled environment at ambient conditions of about 23° C and about 30 to about 60 percent relative humidity. The sample is tested for AUL value at various points throughout an 11-month aging study. The results are set forth in Table 12.

Sample No. 150 represents a carboxymethyl cellulose, Aqualon CMC-7H4F, with no cross-linking agent added. Sample No. 151 represents the material from Table 11 wherein the weight ratio of CMC/Ce<sub>2</sub> (SO<sub>4</sub>)<sub>3</sub> is 100/1 and wherein the CMC is post heat-treated at a temperature of 140° C for 50 minutes. Sample No. 152 represents the material from Table 11 wherein the weight ratio of CMC/Ce<sub>2</sub> (SO<sub>4</sub>)<sub>3</sub> is 100/1 and wherein the CMC is post heat-treated at a temperature of 140° C for 100 minutes. These samples are placed in a temperature and humidity controlled environment. The temperature is maintained at about 23° C and the humidity is maintained at about 100 percent relative humidity. The samples are tested for AUL value at various points throughout an aging study. The results are set forth in Table 13.



TABLE 9

Sample No.	AUL Value (g/g)							
	0 Mins.	5 Mins.	10 Mins.	20 Mins.	25 Mins.	30 Mins.	40 Mins.	50 Mins.
143	10.6	12.4	19.9	21.5	23.1	20.2	18.9	17.4

TABLE 10

Sample No.	AUL Value (g/g)			
	0 days	10 days	20 days	AUL Retention
144	23.1	19.7	17.3	75%
145	20.2	20.5	19.8	98%

TABLE 11

Initial AUL (g/g) at various curing times (min.)

Sample No.	Wt. Ratio CMC/Ce <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0	10	20	30	40	50	60	70	80	100
146	100/1	--	11.7	18.7	22.7	23.2	22.3	21.7	--	16.4	17.3
147	100/2	14.1	22.7	24.0	25.2	22.5	23.3	22.1	20.5	--	--
148	100/3	--	9.95	18.5	20.6	21.0	18.2	18.5	--	15.8	14.9

TABLE 12

AUL Value (g/g)

Sample No.	0 days	3 months	11 months
149	21.7	22.0	18.5

TABLE 13

Sample No.	AUL Value (g/g)		
	0 days	10 days	11 days
150	20.9	9.8	--
151	22.3	--	11.1
152	17.3	--	16.9

TABLE 14

Sample	Additive	Initial		
		Wt. %	Mole%	AUL (g/g)
153	none	0	0	8.4
154	glycolic acid	1	2.87	8.3
155	glycolic acid	2.5	7.16	19.0
156	glycolic acid	5.0	14.32	14.2
157	acetic acid	1.97	7.16	10.7
158	acetic acid	3.94	14.32	16.7
159	acetic acid	5.91	21.48	17.0
160	monochloroacetic acid	0.6	1.38	19.7
161	monochloroacetic acid	1.2	2.76	15.1
162	monochloroacetic acid	3.1	7.16	8.7
163	sodium chloroacetate	0.5	0.93	15.1
164	sodium chloroacetate	1.0	1.87	15.4
165	sodium chloroacetate	2.0	3.74	11.4
166	HCl	0.48	2.87	8.8
167	HCl	0.96	5.74	14.6
168	HCl	1.34	8.61	17.5
169	HCl	2.4	14.32	10.4

**EXAMPLE VII**

Carboxymethyl cellulose (Aqualon CMC-7H4F) is dissolved in distilled water to give 3 weight percent solutions and mixed using a commercial Waring blender run at low speed. Various amounts of acids, based on the weight of CMC used, are added to the solutions. The solutions are spread out in teflon-coated trays and dried at 75° C overnight in a convection oven. After grinding and sieving, the samples are tested for AUL values. The results are set forth in Table 14.

Additional samples, using monochloroacetic acid (MCAA) as a cross-linking additive, are prepared using a similar process used to prepare the samples set forth in Table 14. These samples are placed in a temperature and humidity controlled environment. For Samples 170 and 171, the temperature is maintained at about 23° C and the humidity is maintained at about 100 percent relative humidity. For Samples 172 and 173, the temperature is maintained at about 110° F. (about 43° C) and the humidity is maintained at about 80 percent relative humidity. For Samples 174 and 175, the temperature is maintained at about 23° C and the humidity is maintained at ambient conditions, between about 30 to about 60 percent relative humidity. The samples are tested for AUL value, at 0.3 psi, at various points throughout an aging study. The results are set forth in Table 15.

Various amounts of acetic acid are added to water to achieve a preferred pH. Carboxymethyl cellulose (Aqualon CMC-7H4F) is dissolved in the acidified water to give 3 weight percent CMC solutions and mixed using a commercial Waring blender run at low speed. After the CMC is completely dissolved in the acidified water, the pH of the mixture is measured. This pH value is reported in Table 16. The solutions are spread out in teflon-coated trays, dried at 40° C overnight in a convection oven, and then ground and sieved. A post heat-treatment, at various temperatures and for various lengths of time, is used to additionally cross-link the sam-

TABLE 15

AUL Value (g/g)

Sample No.	wt. ratio MCAA/CMC	0 days	7 days	14 days	33 days	60 days	108 days
170	0.6/100	18.8	16.9	16.75	14.0	9.25	--
171	1.2/100	13.6	13.3	14.63	14.19	--	--
172	0.6/100	18.8	--	--	16.0	15.6	--
173	1.2/100	13.6	--	--	10.5	9.1	--
174	0.6/100	18.8	--	--	--	--	17.0
175	1.2/100	13.6	--	--	--	--	11.4

TABLE 16

AUL Value (g/g)

Sample No.	pH	0 days	15 days	30 days	45 days	60 days	90 days	120 days	150 days	240 days
176	6.8	14.2	--	14.2	14.4	14.4	--	--	16.4	--
177	6.9	16.1	--	16.3	16.5	17.1	--	--	18.1	--
178	7.2	18.1	--	17.9	18.1	17.3	--	--	16.1	--
179	7.4	19.7	--	19.4	19.0	18.2	--	--	15.6	--
180	7.6	21.3	--	19.0	18.9	17.4	--	--	9.5	--
181	6.0	22.1	--	21.3	--	19.8	19.0	16.8	--	15.7
182	7.6	22.3	16.5	11.8	7.6	7.7	6.8	--	--	--

ples. These samples are placed in a temperature and humidity controlled environment. For Samples 176-180, Aqualon CMC-7H4F is used for the carboxymethylcellulose, the heat-treatment conditions used are 140° C for 90 minutes, and the aging conditions used are that the temperature is maintained at about 23° C and the humidity is maintained at ambient conditions, between about 30 to about 60 percent relative humidity. For Samples 181-182, Aqualon CMC-7HCF is used for the carboxymethylcellulose, the heat-treatment conditions used are 100° C for 120 minutes for Sample 181 and 150° C for 35 minutes for Sample 182, and the aging conditions used are that the temperature is maintained at about 23° C and the humidity is maintained at ambient conditions, between about 30 to about 60 percent relative humidity.

#### EXAMPLE VIII

Carboxymethyl cellulose (Aqualon CMC-7H4F) is dissolved in distilled water to give 2 weight percent solutions and mixed using a commercial Hobart mixer run at low to medium speed. Various amounts of an amino acid, aspartic acid (AA), is added to the solutions. The solutions are dried at 80° C overnight in a convection oven. After grinding and sieving, the samples are tested for AUL values at 0.3 psi. A post heat-treatment, at a temperature of 140° C for various lengths of time, is used to additionally cross-link the samples. The samples are again tested for AUL values at about 0.3 psi. The results are set forth in Table 17.

Sample No. 188 represents the material from Table 17 wherein the weight ratio of aspartic acid/CMC is 2.5/100 and wherein the CMC is post heat-treated at a temperature of 110° C for various lengths of time. The samples are tested for AUL value, at 0.3 psi, after the heat-treatment. The results are set forth in Table 18.

Sample No. 189 represents the material from Table 18 wherein the CMC is post heat-treated at a temperature of 110°

TABLE 17  
AUL (g/g) at various curing times

Sample	Weight Ratio AA:CMC	0 min.	5 min.	10 min.	15 min.	20 min.	25 min.	30 min.
183	0:100	7.6	--	24.0	--	24.7	--	24.6
184	0.5:100	9.84	8.34	14.21	18.89	19.11	18.10	18.44
185	1:100	8.40	13.30	20.2	17.73	15.58	14.58	14.05
186	1.5:100	9.36	12.47	16.28	16.39	16.23	15.29	13.53
187	2.5:100	18.21	13.09	9.54	--	--	--	--

TABLE 18  
AUL (g/g) at various curing times

Sample	0 min.	5 min.	10 min.	15 min.	20 min.	25 min.	30 min.
188	18.21	18.09	18.43	18.15	17.90	16.84	16.22

TABLE 19  
AUL Value (g/g)

Sample No.	0 days	5 days	12 days
189	18.43	--	15.51
190	18.15	--	16.20
191	17.90	--	15.21
192	24.4	12.0	--

C for 10 minutes. Sample No. 190 represents the material from Table 18 wherein the CMC is post heat-treated at a temperature of 110° C for 15 minutes. Sample No. 191 represents the material from Table 18 wherein the CMC is post heat-treated at a temperature of 110° C for 20 minutes. Sample No. 192 represents a control material wherein no aspartic acid is added to the CMC and wherein the CMC is post heat-treated at a temperature of 140° C for 30 minutes. These samples are placed in a temperature and humidity controlled environment. The temperature is maintained at about 23° C and the humidity is maintained at about 100 percent relative humidity. The samples are tested for AUL value, at 0.3 psi, at various points throughout an aging study. The results are set forth in Table 19.

#### EXAMPLE IX

Carboxymethyl cellulose (Aqualon CMC-7H4F) is dissolved in distilled water to give 2 weight percent solutions and mixed using a stainless steel mixer with agitator. Various amounts of citric acid (CA), as a cross-linking agent, and sodium hypophosphite (SHP), as a cross-linking catalyst, are added to the solutions. The solutions are mixed well at 25° C, poured into teflon-lined trays, and dried at 95° C for 16 hours in a convection oven. After grinding and sieving to a 300 to 600 micron size fraction, the samples are tested for AUL values at 0.3 psi. The results are set forth in Table 20.

Samples 196, 197, and 199 are also placed in a temperature and humidity controlled environment. The temperature is maintained at about 25° C and the humidity is maintained at about 100 percent relative humidity. The samples are tested for AUL value, at 0.3 psi, at various points throughout an aging study. The results are set forth in Table 21.



**EXAMPLE X**

A general slurry process synthetic scheme is used to prepare samples of carboxymethyl cellulose from cellulose and is described as follows: 15 grams of cellulose is immersed in 400 milliliters of isopropanol in a reaction kettle equipped with a mechanical stirrer, an inert gas inlet, and a temperature control probe. Thirty-five milliliters of water (containing the preferred amount of alkali) is then added. The slurry is stirred for half an hour at room temperature (about 23° C) before adding the appropriate amount of chloroacetic acid (CAA). The reaction is carried out for three hours at 60° C. The slurry is then filtered, the product washed twice with a 70:30 volume-percent mixture (400 ml) of methanol and water, washed once with 400 ml of methanol, and allowed to dry. The recovered carboxymethyl cellulose is then dispersed in water, dried at 30° C, and ground into granules. The particle size fraction between 300 and 600 microns is collected for absorbency testing. The degree of substitution (D.S.) of the carboxymethyl cellulose products is measured by <sup>1</sup>H-NMR spectroscopy. The morphological features of dispersions of the carboxymethyl cellulose products is observed by cross-polarized optical microscopy and X-ray diffraction. The AUL tests are performed at 0.3 psi. The aging tests are accomplished by placing the granular samples into a chamber saturated with water vapor (100 percent relative humidity) at room temperature (about 24° C). At certain intervals of aging time, the samples are taken out of the chamber and dried in ambient conditions for two days before doing the absorbency tests. The unused samples are replaced in the chamber for continued aging.

For the following samples, various cellulose pulps or carboxymethyl celluloses are used, as is indicated in Table 22-24. Aqualon's Cellulose Gum CMC-7H4F is indicated by the designation CMC-7H4F. A cellulose pulp commercially available from ITT Rayonier Corp. under the trade designation

Porosanier-J, is a southern pine wood pulp having an intrinsic viscosity of about 8.4 deciliters/g and having an alpha cellulose content of about 98.7 percent, is indicated by the designation ITT. A cellulose pulp commercially available from Southern Cellulose Products, Inc. under the trade designation Grade 1050, is a cotton linters pulp having an alpha cellulose content of about 99.2 percent, is indicated by the designation SC. A cellulose pulp prepared using a Kraft process without cold caustic treatment after bleaching, having a viscosity of about 15.3 centipoise and an alpha cellulose content of about 94.6 percent, is indicated by the designation CR#8. A cellulose pulp prepared using a Kraft process from a southern softwood chips, wherein sodium hydroxide is used for a cold caustic treatment after bleaching, having a viscosity of about 19.8 centipoise and a degree of polymerization (number average) of about 1477 is indicated by the designation CR#10. A cellulose pulp prepared using a Kraft process from a southern softwood, wherein sodium hydroxide is used for a cold caustic treatment after bleaching, having a viscosity of about 16.6 centipoise and a degree of polymerization (number average) of about 1368 is indicated by the designation CR#11. A cellulose pulp prepared using a Kraft process from aspen chips without cold caustic treatment after bleaching, having a viscosity of about 41.2 centipoise and a degree of polymerization (number average) of about 1997 is indicated by the designation CR#18. The cellulose pulp used to prepare Sample 143 in Table 9 is indicated by the designation CR#21.

For comparison, water-soluble carboxymethyl cellulose samples are synthesized. Table 22 provides the reaction conditions and the absorbency values of the prepared samples. The samples are all soluble in the testing saline solution and the AUL values are for samples aged at ambient temperature (about 24° C) and at about 100 percent relative humidity.

TABLE 20

Sample No.	CA:SHP:CMC wt. ratio	AUL g/g
193	0:0:100	6.9
194	0.3:0.15:100	18.5
195	0.5:0.25:100	19.1
196	0.6:0.30:100	21.3
197	0.7:0.35:100	17.5
198	0.8:0.40:100	14.6
199	1.0:0.50:100	13.6
200	1.5:0.75:100	12.3
201	0.3:0:100	21.1
202	0.6:0:100	18.3
203	1.0:0:100	16.7

TABLE 21

Sample No.	AUL Value (g/g)		
	0 days	12 days	20 days
196	21.3	18.6	18.7
197	17.5	20.1	19.6
199	13.6	15.5	18.6

TABLE 22

Sample	Cellulose	NaOH:CAA Molar Ratio	CAA:Cellulose Molar Ratio	DS	AUL (g/g)		
					0 days	12 days	20 days
204	CMC-7H4F	--	--	0.7-0.8	7.3	7.1	6.5
205	CR#11	2.2:1	0.75:1	0.78	7.1	7.4	8.9
206	ITT	2.0:1	1.0:1	0.96	6.6	8.6	8.8
207	ITT	2.2:1	1.0:1	1.0	8.8	7.6	7.1

Samples are prepared using potassium hydroxide (KOH) as the alkali. Table 23 provides the reaction conditions and the absorbency values of the prepared samples. The samples are all translucent or fibrous when dispersed in water.

As can be seen, for example, by comparing Samples 207 and 212, the use of potassium hydroxide as compared to using sodium hydroxide results in a carboxymethyl cellulose that exhibits both a high initial Absorbency Under Load value and exhibits aging stability.

Sample No. 213 and 214 are prepared using a less than stoichiometric amount of alkali, as indicated by the molar ratio of alkali to chloroacetic acid used being less than 2:1. Sample No. 215 to 222 are prepared using less modifying agent, as indicated by the molar ratio of chloroacetic acid to cellulose used being less than 1:1.

Table 24 provides the reaction conditions and the absorbency values of the prepared samples.

Samples 208 and 214-217 are also placed in a temperature and humidity controlled environment. The temperature is maintained at about 23° C and the humidity is maintained at about 100 percent relative humidity. The samples are tested for AUL value, at 0.3 psi, at various points throughout an aging study. The results are set forth in Table 25.

#### EXAMPLE XI

Carboxymethyl cellulose (Aqualon CMC-7H4F) is dissolved in distilled water to give 2 weight percent solutions and mixed using a commercial Hobart mixer run at low to medium speed. The solutions are dried at 80° C overnight in a convection oven and ground and sieved. A post heat-treatment, at a temperature of 226° C for various lengths of time, is used to cross-link the samples. These samples are placed in a temperature and humidity controlled environment. For Samples 223-228, the temperature is maintained at about 37.8° C and the humidity is maintained at about 80 percent relative humid-

TABLE 23

Sample	Cellulose	KOH:CAA Molar Ratio	CAA:Cellulose Molar Ratio	DS	AUL (g/g)		
					0 days	12 days	20 days
208	CR#8	2.0:1	2.0:1	0.92	14.5	--	--
209	CR#10	2.0:1	1.0:1	0.76	14.3	--	--
210	CR#10	2.0:1	1.5:1	1.13	14.0	--	--
211	ITT	2.2:1	0.75:1	--	13.3	14.4	14.9
212	ITT	2.2:1	1.0:1	--	17.3	16.9	18.4

TABLE 24

Sample	Cellulose	NaOH:CAA Molar Ratio	CAA:Cellulose Molar Ratio	DS	AUL (g/g)		
					0 days	12 days	20 days
213	ITT	1.8:1	0.75:1	0.65	12.6	--	--
214	ITT	1.8:1	1.00:1	0.84	17.2	--	--
215	ITT	2:1	0.75:1	0.76	17.1	--	--
216	ITT	2.2:1	0.60:1	--	17.2	--	--
217	ITT	2.5:1	0.50:1	--	16.2	--	--
218	SC	2.2:1	0.60:1	--	16.1	--	--
219	SC	2.2:1	0.40:1	--	11.8	--	--
220	CR#21	2.2:1	0.50:1	--	19.2	18.7	18.9
221	CR#21	2.2:1	0.40:1	--	13.7	--	--
222	CR#18	2.2:1	0.50:1	--	17.0	--	--

ity. For Samples 229-234, the temperature is maintained at about 25° C and the humidity is maintained at about 100 percent relative humidity. The samples are tested for AUL value, at about 0.3 psi, at various points throughout an aging study. The results are set forth in Table 26.

#### EXAMPLE XII

A sodium carboxymethyl cellulose commercially available from the Aqualon Company under the trade designation Aqualon Cellulose Gum CMC-7HCF or CMC-7H4F is provided. The CMC-7H4F carboxymethyl cellulose has an average degree of substitution of about 0.7 and a viscosity in a 1 percent aqueous solution at about 25° C of about 2500-6000 centipoise. Each carboxymethyl cellulose is dissolved in distilled water to form a solution containing about 2 weight percent carboxymethyl cellulose based on total solution weight. Portions of the solution are then either left at a neutral pH, slightly acidified through the addition of hydrochloric acid (about 0.1 molar aqueous solution) or made basic by the addition of sodium hydroxide (about 0.1 molar aqueous solution). The carboxymethyl cellulose is recovered from the solutions by evaporative drying at about 80° C in an air-convection oven. After drying, the recovered carboxymethyl cellulose is ground into granules in a blender and heat-treated at various times and temperatures in an oven. Various combinations of temperature, time, and solution pH are made, and the samples are then evaluated for AUL values at various times throughout a 60-day aging study. The AUL aging study was conducted at a room temperature of about 24° C and a relative humidity of between about 25 percent to about 45 percent. The preparation process conditions and ° C/min represents the temperature, in degrees Celsius, and time, in minutes, that a sample is heat-treated. In Table 27, Sample Nos. 235-272 employ the CMC-7HCF carboxymethyl cellulose while Sample Nos. 273-279 employ the CMC-7H4F carboxymethyl cellulose.

TABLE 25

Sample No.	AUL Value (g/g)				
	0 days	12 days	40 days	52 days	77 days
208	14.5	14.5	15.1	14.8	14.8
214	17.2	14.6	14.3	--	--
215	17.1	15.0	17.4	--	--
216	17.2	15.8	16.6	--	--
217	16.2	14.8	15.6	--	--

TABLE 26

Sample #	Heat-Treatment Time (sec)	AUL Value (g/g)		
		0 days	10 days	20 days
223	40	22.9	12.8	9.57
224	50	22.6	19.8	11.5
225	60	23.6	19.7	18.4
226	70	18.4	22.3	22.1
227	80	17.2	23.5	21.7
228	90	15.1	20.3	21.9
229	40	22.9	12.8	10.9
230	50	22.6	16.8	11.1
231	60	23.6	20.7	12.8
232	70	18.4	22.2	20.7
233	80	17.2	24.1	21.6
234	90	15.1	22.2	22.1

**EXAMPLE XIII**

Aqualon Cellulose Gum CMC-7H4F carboxymethyl cellulose is dissolved in distilled water to form a solution containing about 2 weight percent carboxymethyl cellulose based on total solution weight. Portions of the solution are then either left at a neutral pH, slightly acidified through the addition of hydrochloric acid (about 0.1 molar aqueous solution) or made basic by the addition of sodium hydroxide (about 0.1 molar aqueous solution). The carboxymethyl cellulose is recovered from the solution by evaporative drying at about 80° C in an air-convection oven. After drying, the recovered carboxymethyl cellulose is ground into granules in a blender and heat-treated at various times and temperatures in an oven. Various combinations of temperature, time, and solution pH are made, and the samples are then evaluated for AUL values at various times throughout a 60-day aging study. The AUL aging study was conducted at a room temperature of about 24° C and a relative humidity of between about 25 percent to about 45 percent. The preparation process conditions and the AUL values of the various samples are set forth in Table 28. The listed pH is for the solution of carboxymethyl cellulose and water prior to recovery of the carboxymethyl cellulose. In Table 28, ° C/min represents the temperature, in degrees Celsius, and time, in minutes, that a sample is heat-treated.

**EXAMPLE XIV**

In Examples XIV through XVII an aging study was conducted on the carboxymethyl cellulose superabsorbent materials prepared according to the Examples XIV through XVII. The results are presented in Tables 29-33 and show the superabsorbents prepared in accordance with Examples XIV through XVII do not exhibit at least 50% retention of the initial AUL after being aged in 100% relative humidity for 60 days.

A sodium carboxymethyl cellulose commercially available from the Aqualon Company under the trade designation Aqualon™



Table 27

5	Sample No.	pH(DA)	Heating (°C/min)	0 days	AUL (q/q of the aged Samples)					
					10 days	20 days	30 days	40 days	50 days	60 days
10	235	6.08(3)	N.A.	10.7	---	---	---	---	---	---
	236	6.08(3)	140/5	17.1	17.3	15.4	13.6	14.1	12.9	13.5
	237	6.08(3)	140/8	15.3	15.9	16.1	16.7	16.8	15.7	15.8
	238	6.08(3)	140/10	13.2	14.2	15.3	14.9	14.6	14.7	15.8
	239	6.08(3)	140/20	11.0	12.1	13.1	12.8	13.0	13.6	13.2
	240	6.08(3)	140/30	9.2	9.8	9.3	9.6	10.3	11.4	12.5
15	241	6.44(.5)	N.A.	7.8	---	---	---	---	---	---
	242	6.44(.5)	120/60	18.2	17.2	13.2	11.4	10.7	10.2	9.7
	243	6.44(.5)	140/10	17.2	18.1	16.1	15.3	15.6	15.7	14.0
	244	6.44(.5)	140/20	21.5	19.0	18.0	18.1	16.1	17.3	15.6
	245	6.44(.5)	140/30	24.3	20.3	19.3	19.0	17.4	16.5	14.3
	246	6.44(.5)	140/40	20.9	19.5	19.9	19.4	18.9	17.1	15.9
20	247	6.44(.5)	140/50	18.3	18.7	19.3	18.9	18.3	18.5	18.0
	248	6.44(.5)	150/10	18.6	19.1	18.7	18.6	16.3	14.6	14.7
	249	6.44(.5)	150/15	22.1	19.9	19.7	20.1	18.9	16.2	15.8
	250	6.44(.5)	150/20	21.4	20.3	19.5	19.0	19.6	18.4	18.1
	251	6.44(.5)	150/30	16.4	16.5	16.3	16.1	17.5	16.9	16.7
	252	7.4(0)	N.A.	6.5	---	---	---	---	---	---
25	253	7.4(0)	130/90	24.6	20.1	17.1	15.4	11.7	10.5	9.8
	254	7.4(0)	150/30	26.9	23.0	19.9	20.1	17.1	13.0	12.8
	255	7.4(0)	150/40	24.5	21.3	20.1	18.3	16.0	14.1	13.6
	256	7.4(0)	150/45	25.1	20.9	17.9	16.0	13.4	14.7	12.8
	257	7.4(0)	150/50	26.8	22.4	19.3	17.1	13.1	13.9	13.0
	258	7.4(0)	150/60	25.0	21.8	20.4	19.6	17.8	14.5	15.1
30	259	7.4(0)	150/75	24.8	20.9	21.5	20.7	19.2	19.3	17.8
	260	7.4(0)	150/90	22.9	20.1	20.8	19.8	18.3	18.6	17.3
	261	7.4(0)	150/120	20.5	20.8	19.3	20.5	17.5	17.8	16.9
	262	8.92	N.A.	6.8	---	---	---	---	---	---
	263	8.92	150/40	10.1	10.2	9.2	10.4	8.1	7.6	---
	264	8.92	150/80	14.2	13.6	10.1	9.4	8.1	8.3	---
35	265	8.92	150/100	15.0	14.8	11.0	8.4	8.5	7.9	---
	266	8.92	150/120	15.5	15.1	12.9	10.7	9.7	8.9	---
	267	8.92	150/150	16.3	15.7	13.4	11.0	10.9	10.5	---
	268	10.72	N.A.	5.1	---	---	---	---	---	---
	269	10.72	150/50	6.2	6.3	6.4	6.2	6.5	---	---
	270	10.72	150/100	6.8	6.7	6.8	6.1	6.4	---	---
40	271	10.72	150/150	7.1	6.5	6.4	6.3	6.0	---	---
	272	10.72	150/200	7.0	7.1	6.8	6.5	6.7	---	---
	273	7.4(0)	N.A.	8.3	---	---	---	---	---	---
	274	7.4(0)	150/8	24.1	20.1	19.1	17.3	14.5	11.2	8.1
	275	7.4(0)	150/10	26.8	21.9	20.0	18.4	15.3	12.0	9.8
	276	7.4(0)	150/12	28.2	22.3	22.1	20.8	16.1	13.9	12.1
50	277	7.4(0)	150/15	27.5	21.8	20.9	20.7	17.8	15.1	15.7
	278	7.4(0)	150/20	25.1	24.9	22.6	19.8	18.1	14.7	14.0
	279	7.4(0)	150/60	19.9	19.8	20.1	19.2	17.8	18.1	17.9

Table 28

5	Sample No.	pH	Heating (°C/min)	0 days	AUL (q/q of the aged Samples)					
					10 days	20 days	30 days	40 days	50 days	60 days
10	280	3.5	120/10	16.5	16.1	16.0	16.1	16.0	16.7	16.3
	281	3.5	120/20	14.3	14.9	14.8	14.7	14.6	14.0	15.3
	282	3.5	120/30	11.9	12.0	12.3	12.5	12.7	13.3	13.7
	283	4.0	120/10	18.9	17.3	18.3	18.2	18.0	18.4	17.6
	284	4.0	120/20	21.5	22.9	21.8	21.9	21.4	21.5	21.9
	285	4.0	120/30	19.3	20.8	20.7	21.0	20.7	21.3	21.8
15	286	7.0	140/70	21.3	20.6	18.1	19.3	18.5	17.1	17.3
	287	7.0	140/80	20.1	20.6	19.9	20.9	19.6	19.8	19.2
	288	7.0	140/90	18.9	19.3	19.2	20.1	20.7	20.1	20.0
	289	7.0	200/1	20.6	20.1	20.3	19.9	19.7	18.9	18.5
	290	7.0	200/2	18.1	18.6	18.7	19.3	19.6	19.5	18.9
	291	7.0	200/5	11.6	12.3	15.6	16.4	16.9	17.3	17.1
20	292	7.4	140/70	22.6	21.9	17.3	17.1	16.5	13.7	13.9
	293	7.4	140/80	21.9	21.8	18.9	19.3	18.4	17.9	18.3
	294	7.4	140/90	20.8	20.9	20.4	20.6	20.5	19.8	20.2
	295	7.4	200/1	22.4	21.5	18.7	18.6	18.7	18.0	17.4
	296	7.4	200/2	19.2	20.5	19.6	20.3	19.4	20.1	19.8
	297	7.4	200/5	13.0	14.5	15.1	16.8	17.5	18.3	18.1
25	298	7.6	140/70	23.9	22.1	16.6	10.1	8.9	8.6	9.1
	299	7.6	140/80	22.6	22.0	19.0	15.4	13.2	10.7	11.5
	300	7.6	140/90	21.5	21.4	20.9	17.8	16.1	14.1	14.8
	301	7.6	200/1	23.8	22.6	20.1	18.9	16.5	12.8	8.3
	302	7.6	200/2	20.6	20.8	19.2	19.6	18.4	17.0	16.2
	303	7.6	200/5	14.1	15.6	15.9	15.7	16.3	17.1	16.8

Table 29.

Sample #	pH(DA)	Heat Treatment	Aging RH	AUL (g/g) in 0.9% NaCl						
				0 Day	10 Days	20 Days	30 Days	40 Days	50 Days	60 Days
N 1	6.08(3)	N.A.	60%	10.1	9.8	8.1	7.2	7.2	7.3	6.5
			100%	10.1	7.0	5.6	5.7	5.6	5.9	5.8
N 2	6.08(3)	140°Cx5 min	60%	16.7	10.3	9.0	7.6	6.9	7.2	7.0
			100%	16.7	7.4	6.1	5.3	4.7	5.6	5.3
N 3	6.08(3)	140°Cx8 min	60%	16.1	11.6	8.3	8.1	7.9	8.3	8.1
			100%	16.1	8.4	7.0	5.9	6.2	6.7	5.8
N 4	6.08(3)	140°Cx10 min	60%	14.1	12.4	9.2	8.4	8.3	7.8	7.9
			100%	14.1	8.7	8.0	7.3	7.0	7.3	7.2
N 5	6.08(3)	140°Cx20 min	60%	12.4	9.1	8.5	8.6	8.4	8.0	7.6
			100%	12.4	9.9	8.0	7.4	7.5	7.1	7.3
N 6	6.08(3)	140°Cx30 min	60%	10.5	8.7	7.5	7.0	6.7	7.1	7.2
			100%	10.5	7.9	8.1	8.2	8.0	7.5	7.4
N 7	6.44(0.5)	N.A.	60%	7.9	7.3	7.4	7.0	7.3	7.1	6.8
			100%	7.9	5.6	5.7	5.4	5.6	5.1	5.0
N 8	6.44(0.5)	120°Cx60 min	60%	17.5	15.3	13.2	10.2	10.0	9.7	9.4
			100%	17.5	10.1	8.1	6.3	7.0	6.7	6.3
N 9	6.44(0.5)	140°Cx10 min	60%	18.2	14.7	12.9	9.3	9.2	9.5	9.4
			100%	18.2	11.1	8.0	5.7	5.0	5.2	5.2
N 10	6.44(0.5)	140°Cx20 min	60%	20.9	15.3	13.1	10.7	10.8	10.1	10.2
			100%	20.9	13.7	11.3	7.1	7.3	7.0	6.8
N 11	6.44(0.5)	140°Cx30 min	60%	23.6	15.9	12.8	12.0	11.7	11.9	11.5
			100%	23.6	15.1	9.2	7.8	7.5	7.8	7.4
N 12	6.44(0.5)	140°Cx40 min	60%	22.1	14.8	11.7	10.6	10.7	10.2	9.5
			100%	22.1	13.2	11.9	8.1	8.4	8.4	7.5
N 13	6.44(0.5)	140°Cx50 min	60%	19.8	14.5	12.7	10.4	11.2	10.6	9.3
			100%	19.8	12.1	8.3	7.1	6.7	6.3	6.4
N 14	6.44(0.5)	150°Cx10 min	60%	18.5	10.0	9.1	7.4	7.8	7.2	7.3
			100%	18.5	8.1	7.3	6.2	5.8	6.3	6.1
N 15	6.44(0.5)	150°Cx15 min	60%	21.9	13.4	11.0	9.3	9.3	8.7	8.9

Table 29. (continued)

			100%	21.9	10.2	6.8	5.6	5.8	5.2	5.4
N16	6.44(0.5)	150°Cx20 min	60%	20.8	14.7	13.2	10.8	10.0	9.8	9.5
			100%	20.8	11.0	7.3	5.9	6.1	6.2	5.8
N17	6.44(0.5)	150°Cx30 min	60%	17.8	14.9	12.5	9.3	9.2	8.7	8.8
			100%	17.8	10.3	8.3	6.9	6.3	6.5	6.3
N18	7.44(0)	N.A.	60%	5.8	5.6	5.8	5.4	5.2	5.1	5.3
			100%	5.8	5.2	5.3	5.0	5.1	4.9	4.8
N19	7.44(0)	130°Cx70 min	60%	23.7	16.2	12.8	11.7	11.3	10.7	10.1
			100%	23.7	12.8	9.1	7.2	7.4	7.0	6.8
N20	7.44(0)	150°Cx30 min	60%	25.7	17.5	13.1	12.6	12.1	11.5	10.7
			100%	25.7	14.1	9.2	7.8	7.6	7.2	7.4
N21	7.44(0)	150°Cx40 min	60%	25.1	17.9	14.2	12.9	12.1	12.3	11.5
			100%	25.1	13.8	8.9	6.8	6.9	7.1	6.5
N22	7.44(0)	150°Cx45 min	60%	24.8	16.7	14.6	13.5	12.1	12.5	11.7
			100%	24.8	14.1	8.5	7.6	7.4	7.8	7.2
N23	7.44(0)	150°Cx50 min	60%	25.9	15.0	12.7	10.3	9.8	9.2	9.3
			100%	25.9	13.7	9.2	6.9	6.7	6.1	6.3
N24	7.44(0)	150°Cx60 min	60%	24.3	16.4	15.2	13.2	12.7	12.4	11.9
			100%	24.3	12.1	8.6	7.0	6.8	6.3	6.1
N25	7.44(0)	150°Cx75 min	60%	23.9	15.7	14.1	12.9	12.1	12.4	12.1
			100%	23.9	13.0	9.4	7.8	7.1	7.2	6.5
N26	7.44(0)	150°Cx90 min	60%	22.1	17.3	15.0	14.8	13.2	12.6	11.0
			100%	22.1	14.2	8.9	6.8	6.4	6.1	5.7
N27	7.44(0)	150°Cx120min	60%	19.6	16.7	14.3	12.8	11.5	11.7	12.1
			100%	19.6	13.8	10.3	8.5	7.3	7.0	7.2
N28	8.92	N.A.	60%	6.1	6.4	6.0	6.3	6.1	6.3	6.2
			100%	6.1	6.2	5.8	5.7	5.2	5.0	4.6
N29	8.92	150°Cx40 min	60%	9.7	7.0	6.8	7.1	6.5	6.0	6.1
			100%	9.7	6.2	5.3	5.4	5.3	5.0	4.7
N30	8.92	150°Cx80 min	60%	13.6	8.1	7.0	6.7	6.1	6.4	6.3
			100%	13.6	7.1	6.3	6.4	5.6	5.3	5.4
N31	8.92	150°Cx100min	60%	14.3	8.2	7.4	7.6	7.2	6.9	6.8
			100%	14.3	6.7	7.1	6.5	5.2	4.9	4.7
N32	8.92	150°Cx120min	60%	15.1	10.2	7.8	7.6	7.2	7.3	6.9
			100%	15.1	6.9	7.0	7.2	6.7	6.9	6.2
N33	8.92	150°Cx150min	60%	15.6	9.8	8.7	8.1	7.8	6.9	7.3
			100%	15.6	7.3	5.8	6.2	5.8	6.2	6.0
N34	10.72	N.A.	60%	4.3	4.5	4.2	4.5	4.2	4.5	4.6
			100%	4.3	4.2	4.1	4.3	4.1	4.0	4.2
N35	10.72	150°Cx50 min	60%	5.6	5.2	5.3	5.0	5.1	5.4	5.2

Table 29 (continued)

			100%	5.6	5.1	4.5	4.7	4.8	4.5	4.1
N36	10.72	150°Cx100min	60%	5.9	6.0	5.8	5.3	5.3	5.4	5.6
			100%	5.9	5.0	5.2	4.8	4.3	4.8	4.6
N37	10.72	150°Cx150min	60%	6.3	6.2	6.0	6.2	6.0	5.8	5.9
			100%	6.3	5.8	5.3	5.4	5.0	4.7	4.8
N38	10.72	150°Cx200min	60%	6.0	5.7	6.0	5.8	5.9	6.0	5.3
			100%	6.0	4.7	5.1	4.9	4.6	5.0	4.1
N39	(0)	N.A.	60%	7.1	7.3	7.0	7.4	7.2	6.8	7.3
			100%	7.1	6.3	6.7	5.8	5.3	5.6	4.8
N40	(0)	150°Cx8 min	60%	7.9	6.8	7.1	7.1	6.7	6.3	6.6
			100%	7.9	5.7	5.6	5.9	5.6	5.7	5.2
N41	(0)	150°Cx10 min	60%	23.1	14.1	10.9	8.3	7.9	8.4	8.1
			100%	23.1	8.2	6.4	6.5	6.2	6.0	5.7
N42	(0)	150°Cx12 min	60%	25.7	16.3	11.5	9.2	8.9	9.0	8.6
			100%	25.7	10.7	8.5	8.0	7.9	8.1	7.7
N43	(0)	150°Cx15 min	60%	27.9	18.9	15.3	13.1	12.3	12.7	12.0
			100%	27.9	16.1	8.9	9.3	8.1	7.0	6.2
N44	(0)	150°Cx20 min	60%	26.1	18.0	16.7	14.2	12.5	11.9	12.3
			100%	26.1	15.6	10.2	8.7	7.8	6.2	6.5
N45	(0)	150°Cx60 min	60%	24.0	17.4	16.2	13.9	13.6	12.0	12.5
			100%	24.0	13.7	10.1	7.8	6.3	6.4	6.2

Note: Samples #1 to #38 used Aqualon CMC-7HCF (lot#69374) and #39 to #45 CMC-7H4F (lot#73899).

Table 30

Sample No.	DA (mol%)	Treatment	Aging RH	AUL (g/g) in 0.9% NaCl						
				0 Day	10 Days	20 Days	30 Days	40 Days	50 Days	60 Days
N46	3	150Cx30min	100%	10.1	11.2	9.8	9.5	9.6	8.2	6.4
N47	0.5	N/A	100%	7.0	6.1	5.7	5.3	5.4	5.3	5.4
N48	0.5	150Cx5min	100%	17.5	10.2	8.3	7.1	6.0	5.3	5.5
N49	0.5	150Cx8min	100%	21.5	13.2	10.2	8.7	6.9	5.6	5.3
N50	0.5	150Cx10min	100%	22.5	16.3	12.1	9.8	7.2	6.1	5.7
N51	0.5	150Cx15min	100%	21.4	17.1	14.2	10.2	8.7	7.2	6.1
N52	0.5	150Cx20min	100%	19.3	16.3	13.2	11.2	10.6	8.6	6.2
N53	0.5	150Cx30min	100%	15.8	12.7	10.9	9.5	8.2	7.8	6.7
N54	0.1	N/A	100%	7.3	6.0	5.3	5.4	5.2	5.3	5.3
N55	0.1	150Cx10min	100%	11.3	8.7	6.0	5.1	5.1	5.1	5.0
N56	0.1	150Cx20min	100%	20.8	14.5	10.7	8.5	5.7	5.4	5.5
N57	0.1	150Cx30min	100%	22.3	16.2	12.0	10.2	8.3	6.1	6.2
N58	0.1	150Cx40min	100%	21.3	17.2	13.4	10.5	9.4	7.6	7.1
N59	0.1	150Cx60min	100%	19.2	15.2	13.4	11.2	10.2	9.1	8.2
N60	0	N/A	100%	7.4	6.2	5.5	5.3	5.0	5.2	5.1
N61	0	130Cx60min	100%	9.1	7.1	6.2	5.0	5.1	5.1	5.0
N62	0	130Cx90min	100%	14.3	9.0	7.4	6.2	6.0	5.6	5.7
N63	0	130Cx120min	100%	19.7	12.1	9.0	7.4	7.2	7.0	6.3
N64	0	130Cx150min	100%	21.6	14.2	10.8	8.7	8.1	7.8	7.3
N65	0	N/A	100%	7.4	6.2	5.5	5.3	5.0	5.2	5.1
N66	0	170Cx10min	100%	18.7	14.2	10.0	9.1	7.8	6.8	6.4
N67	0	170Cx20min	100%	12.9	10.6	10.1	9.8	8.8	8.1	8.0
N68	0	170Cx30min	100%	10.7	10.1	9.9	8.9	9.2	9.0	8.7

Note: Samples #46 to #68 used Aqualon CMC-9H4F (lot#73888)

Table 31

<u>Sample No.</u>	<u>DA (mol%)</u>	<u>Treatment</u>	<u>Aging RH</u>	<u>AUL (g/g) in 0.9% NaCl</u>						
				<u>0</u> <u>Day</u>	<u>10</u> <u>Days</u>	<u>20</u> <u>Days</u>	<u>30</u> <u>Days</u>	<u>40</u> <u>Days</u>	<u>50</u> <u>Days</u>	<u>60</u> <u>Days</u>
N 69	0	N/A	100%	7.4	6.2	5.5	5.3	5.0	5.2	5.1
N 70	0	150Cx20min	100%	20.3	12.0	8.6	7.1	7.0	7.1	6.9
N 71	0	150Cx30min	100%	23.5	15.2	12.1	12.5	10.1	8.8	8.0
N 72	0	150Cx40min	100%	25.2	13.4	12.8	11.1	9.0	8.9	9.1
N 73	0	150Cx50min	100%	20.9	16.5	14.0	12.1	8.9	9.2	8.7
N 74	0	N/A	100%	7.4	6.2	5.5	5.3	5.0	5.2	5.1
N 75	0	150Cx10min	100%	8.9	7.0	7.1	7.2	6.8	6.7	6.8
N 76	0	150Cx15min	100%	16.4	9.1	8.0	7.5	7.6	7.3	6.7
N 77	0	150Cx20min	100%	24.6	15.2	12.0	8.9	7.2	7.5	7.0
N 78	0	150Cx30min	100%	22.5	14.3	11.7	10.1	9.2	8.7	8.0
N 79	0	150Cx45min	100%	21.5	14.7	12.3	10.8	10.1	9.4	8.5
N 80	0	150Cx60min	100%	17.9	12.0	9.8	8.7	8.0	7.9	8.2

Note: Samples #46 to #68 used Aqualon CMC-9H4F (lot#73888)

Table 32

<u>Sample No.</u>	<u>DA (mol%)</u>	<u>Treatment</u>	<u>Aging RH</u>	<u>AUL (g/g) in 0.9% NaCl</u>						
				<u>0</u> <u>Day</u>	<u>10</u> <u>Days</u>	<u>20</u> <u>Days</u>	<u>30</u> <u>Days</u>	<u>40</u> <u>Days</u>	<u>50</u> <u>Days</u>	<u>60</u> <u>Days</u>
N 81	0	N/A	100%	7.3	6.1	5.8	5.6	5.3	5.6	5.4
N 82	0	150Cx20min	100%	20.1	10.1	7.8	6.8	6.0	5.7	5.9
N 83	0	150Cx30min	100%	19.3	12.4	8.7	6.7	5.9	5.8	6.1
N 84	0	150Cx40min	100%	19.1	13.2	10.2	8.6	7.2	6.4	6.0

Note: Samples #46 to #68 used Aqualon CMC-9H4F (lot#73888)

Table 33

<u>Sample No.</u>	<u>DA (mol%)</u>	<u>Treatment</u>	<u>Aging RH</u>	<u>AUL (g/g) in 0.9% NaCl</u>						
				<u>0</u> <u>Day</u>	<u>10</u> <u>Days</u>	<u>20</u> <u>Days</u>	<u>30</u> <u>Days</u>	<u>40</u> <u>Days</u>	<u>50</u> <u>Days</u>	<u>60</u> <u>Days</u>
N 85		150Cx15min	100%	6.7	5.5	5.5	5.6	5.3	5.4	5.2
N 86		150Cx60min	100%	6.3	5.2	5.4	5.3	5.3	5.2	5.3

Note: Samples #85 used Aqualon CMC-7HCF (lot#69374) and Sample #86 used Aqualon CMC-9H4F (lot#73888)

Cellulose Gum CMC-7HCF or CMC-7H4F is provided. The carboxymethyl cellulose has an average degree of substitution of 0.7. CMC-7H4F has a slightly higher molecular weight than the CMC-7HCF. The carboxymethyl cellulose is dissolved in distilled water to form a solution containing 2 weight percent carboxymethyl cellulose based on total solution weight. The solution is then either left at a neutral pH, slightly acidified through the addition of hydrochloric acid (0.1 molar aqueous solution) or made basic by the addition of sodium hydroxide (0.1 molar aqueous solution). The carboxymethyl cellulose is recovered from the solution by evaporative drying at 80° C in a Blue M air-convection oven. After drying, the recovered carboxymethyl cellulose is ground into granules in a blender and heat-treated at various times and temperatures in an oven. Various combinations of temperature, time, and solution pH are made, and the physical properties of the resultant carboxymethyl cellulose determined. The exact process conditions and the physical properties of the resultant carboxymethyl cellulose are set forth in Table 29. Sample Nos. No-38 employ the CMC-7HCF while Samples Nos. N39-45 employ the CMC-7H4F. pH is noted of the solution of carboxymethyl cellulose and water prior to recovery (Degree of Molar Acidification). Absorbency Under Load is noted in grams absorbed aqueous saline solution (0.9 weight percent) per gram of carboxymethyl cellulose under a load of 0.3 psi.

#### EXAMPLE XV

Example XIV is repeated with the exception that a sodium carboxymethyl cellulose commercially available from the Aqualon Company under the trade designation Aqualon™ Cellulose Gum CMC-9H4 is employed. The carboxymethyl cellulose has an average degree of substitution of 0.9. The exact process conditions and physical properties of the resultant carboxymethyl cellulose are set forth in Table 30.



**EXAMPLE XVI**

Example XV is repeated with the exception that the carboxymethyl cellulose is recovered and comminuted to form both granules and flakes. The carboxymethyl cellulose is then heat-treated at 150° C for various times to determine the effect of geometry on the heat-treatment process. The results are set forth in Table 31. Samples N69-73 are in granular form. Samples N74-80 are in the form of flakes.

**EXAMPLE XVII**

Example XV is repeated with the exception that the carboxymethyl cellulose is dissolved in distilled water to form a solution containing 23 weight percent carboxymethyl cellulose based on total solution weight. The recovered carboxymethyl cellulose is heat-treated in the form of granules at 150° C for various time periods. The physical properties of the resultant polymer are set forth in Table 32.

Control samples of the carboxymethyl cellulose of Example XIV and Example XV in which the carboxymethyl cellulose is subjected to a heat-treatment process without having been dissolved in an aqueous solution and recovered were performed. The exact process conditions of the heat-treatment step and the physical properties of the resultant polymer are set forth in Table 33. Both control samples remain water soluble even after the heat-treatment step.

While the present invention has been described in terms of the specific embodiments, numerous equivalent changes and modifications will be apparent from the detailed description. Accordingly, the specific examples set forth above are not intended to limit in any manner the scope of the invention as set forth in the appended claims.

WHAT IS CLAIMED IS:

1. A method for providing a natural-based material having preferred absorbency under load and preferred aging characteristics, comprising:

- a) providing an aqueous mixture of water-soluble carboxyalkyl polysaccharide, wherein said water-soluble carboxyalkyl polysaccharide is dissolved in water;
- b) recovering carboxyalkyl polysaccharide from said aqueous mixture to form a recovered carboxyalkyl polysaccharide;
- c) heat-treating said recovered carboxyalkyl polysaccharide at a temperature above about 50° C to form a carboxyalkyl polysaccharide which is water swellable and water insoluble, wherein said water-swellable, water-insoluble carboxyalkyl polysaccharide has an initial Absorbency Under Load value of at least 17; and
- d) retaining at least 50 percent of the initial Absorbency Under Load value after being aged under at least about 60 percent relative humidity for 60 days at 24° C.

2. A method for providing a natural-based material having preferred absorbency under load and preferred aging characteristics as set forth in Claim 1, wherein said aqueous mixture of water-soluble carboxyalkyl polysaccharide has a pH between about 4.0 and about 7.5.

3. A method for providing a natural-based material having preferred absorbency under load and preferred aging characteristics as set forth in Claim 1, wherein said retaining step comprises aging said water-swellable, water-insoluble carboxyalkyl polysaccharide under at least about 60 percent relative humidity comprises aging for about 60 days at about 24° C.

4. A method for providing a natural-based material having preferred absorbency under load and preferred aging character-

istics as set forth in Claim 1, wherein said aging comprises aging under at least about 80 percent relative humidity.

5. A method for providing a natural-based material having preferred absorbency under load and preferred aging characteristics as set forth in Claim 1, wherein said aging comprises aging under about 100 percent relative humidity.

6. A method for providing a natural-based material having preferred absorbency under load and preferred aging characteristics as set forth in Claim 1, wherein said heat treating comprises heat-treating said recovered carboxyalkyl polysaccharide at a temperature above about 50° C for a time effective to cross link and form a carboxyalkyl polysaccharide which is water swellable and water insoluble.

7. A method for providing a natural-based material having preferred absorbency under load and preferred aging characteristics as set forth in Claim 1, wherein said aqueous mixture of water-soluble carboxyalkyl polysaccharide comprises a homogeneous mixture.

8. A method for providing a natural-based material having preferred absorbency under load and preferred aging characteristics as set forth in Claim 1, wherein said carboxyalkyl polysaccharide is prepared from a polysaccharide selected from the group consisting of cellulose, starch, guar, carrageenan, agar, gellan gum, chitin, chitosan, and mixtures of cellulose, starch, guar, carrageenan, agar, gellan gum, chitin, chitosan

9. A method for providing a natural-based material having preferred absorbency under load and preferred aging characteristics as set forth in Claim 1, wherein said carboxyalkyl polysaccharide is a carboxymethyl polysaccharide.

10. A method for providing a natural-based material having preferred absorbency under load and preferred aging characteristics as set forth in Claim 1, wherein said carboxyalkyl polysaccharide is a carboxymethyl cellulose.

11. A method for providing a natural-based material having preferred absorbency under load and preferred aging characteristics as set forth in Claim 1, wherein said carboxyalkyl polysaccharide is recovered by evaporative drying.

12. A method for providing a natural-based material having preferred absorbency under load and preferred aging characteristics as set forth in Claim 1, wherein said water-swellaable, water-insoluble carboxyalkyl polysaccharide exhibits an initial Absorbency Under Load value of at least about 20.

13. A method for providing a natural-based material having preferred absorbency under load and preferred aging characteristics as set forth in Claim 1, wherein said water-swellaable, water-insoluble carboxyalkyl polysaccharide retains at least about 70 percent of the initial Absorbency Under Load value after aging for about 60 days at about 23° C and at least about 60 percent relative humidity.

14. A method for providing a natural-based material having preferred absorbency under load and preferred aging characteristics as set forth in Claim 1, wherein said water-swellaable, water-insoluble carboxyalkyl polysaccharide retains at least about 50 percent of the initial Absorbency Under Load value after aging for about 60 days at about 23° C and at about 100 percent relative humidity.

15. A method for providing a natural-based material having preferred absorbency under load and preferred aging characteristics as set forth in Claim 2, wherein said aqueous mixture

of water-soluble carboxyalkyl polysaccharide has a pH between about 6.0 and about 7.5.

16. A method for providing a natural-based material having preferred absorbency under load and preferred aging characteristics as set forth in Claim 5, wherein said aging comprises aging under at least about 60 percent relative humidity for about 60 days at about 24° C.

17. A method for providing a natural-based material having preferred absorbency under load and preferred aging characteristics as set forth in Claim 6, wherein said carboxyalkyl polysaccharide is heat-treated at a temperature of from about 100° C to about 200° C for a time of from about 1 minute to about 600 minutes.

18. A water-swellaable, water-insoluble carboxyalkyl polysaccharide, comprising a carboxyalkyl polysaccharide having an initial Absorbency Under Load value of at least 17 and having an Absorbency Under Load after 60 days of at least about 50 percent of the initial Absorbency Under Load, formed by providing an aqueous mixture of water-soluble carboxyalkyl polysaccharide, wherein said water-soluble carboxyalkyl polysaccharide is dissolved in water at a pH between about 4.0 and about 7.5; recovering carboxyalkyl polysaccharide from said aqueous mixture to form a recovered carboxyalkyl polysaccharide; and heat-treating said recovered carboxyalkyl polysaccharide at a temperature above about 50° C to form a carboxyalkyl polysaccharide which is water swellaable and water insoluble.

19. A water-swellaable, water-insoluble carboxyalkyl polysaccharide as set forth in Claim 18 having an Absorbency Under Load of at least about 50 percent of the initial Absorbency

Under Load after 60 days under 100 percent relative humidity at about 24° C.

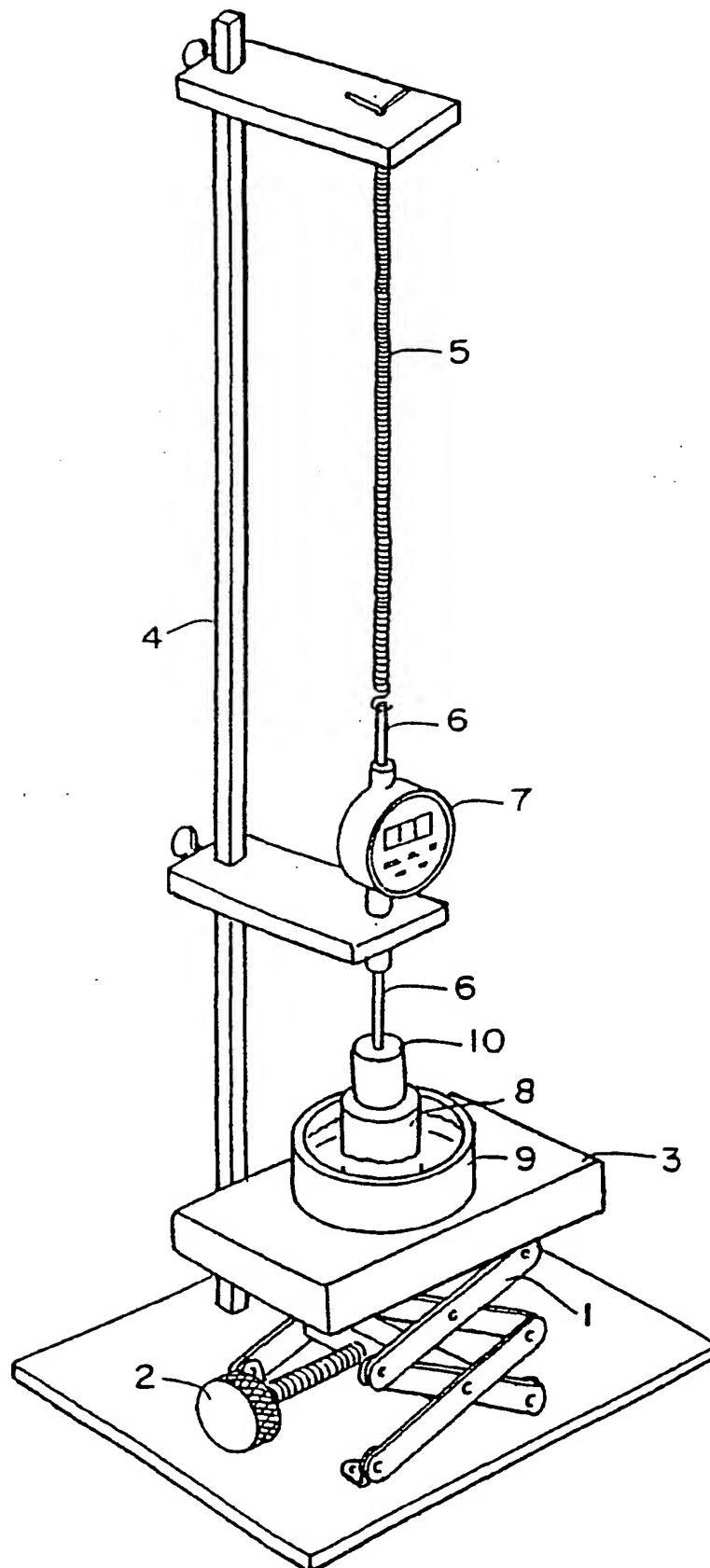
20. A method for providing a natural-based material having preferred absorbency under load and preferred aging characteristics, comprising:

a) providing an aqueous homogeneous mixture of water-soluble carboxyalkyl polysaccharide, wherein said water-soluble carboxyalkyl polysaccharide is dissolved in water at a pH between about 6.0 and about 7.5.;

b) recovering carboxyalkyl polysaccharide from said aqueous mixture by evaporative drying to form a recovered carboxyalkyl polysaccharide;

c) heat-treating said recovered carboxyalkyl polysaccharide at a temperature from about 100° C to about 200° C for a time of from about 5 minutes to about 100 minutes to form a carboxyalkyl polysaccharide which is water swellable and water insoluble, wherein said water-swellable, water-insoluble carboxyalkyl polysaccharide has an initial Absorbency Under Load value of at least 20; and

d) retaining at least 70 percent of the initial Absorbency Under Load value after being aged under at least about 60 percent relative humidity for 60 days at 24° C.



FIGURE

**(19) World Intellectual Property Organization  
International Bureau**



**(43) International Publication Date**  
**22 November 2001 (22.11.2001)**

PCT

**(10) International Publication Number**  
**WO 01/87365 A3**

**(51) International Patent Classification<sup>7</sup>:** C08B 11/20.  
15/00, 37/00, A61L 15/00, 15/28

**(72) Inventor; and**

(75) **Inventor/Applicant (for US only):** QIN, Jian [US/US];  
1602 East Cranberry Drive, Appleton, WI 54915 (US).

**(21) International Application Number:** PCT/US01/12761

(74) Agent: **GLANTZ, Douglas**: 5260 Deborah Court,  
Doylstown, PA 18901-1949 (US).

(22) International Filing Date: 19 April 2001 (19.04.2001)

(25) Filing Language: English

(26) Publication Language: English

**(30) Priority Data:**  
09/572,492 15 May 2000 (15.05.2000) US

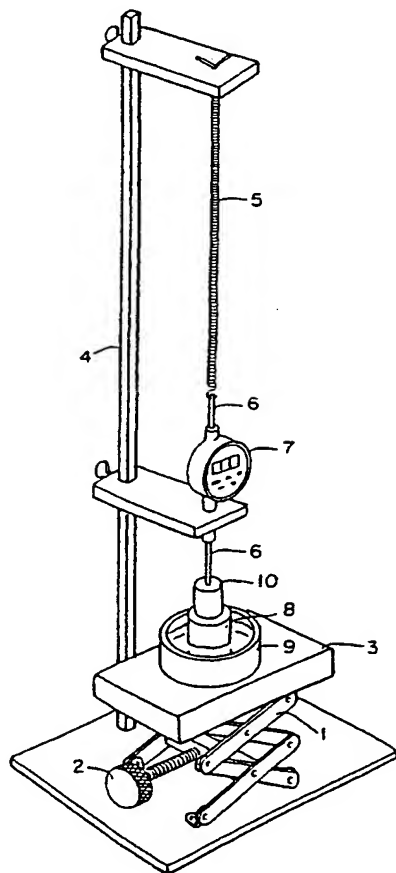
**(81) Designated States (national):** AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(71) **Applicant** (for all designated States except US): **KIMBERLY-CLARK WORLDWIDE, INC.** [US/US]; 401 North Lake Street, Neenah, WI 54956 (US).

**(84) Designated States (regional):** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,

*[Continued on next page]*

**(54) Title: POLYSACCHARIDE ABSORBENT AND METHOD**



**(57) Abstract:** Disclosed are novel polysaccharide absorbents and method for providing a water-swellaable, water-insoluble modified polysaccharide having preferred age-stable absorption properties. The novel polysaccharide absorbents and method provide a natural-based absorbent and preferred aging characteristics for absorbency. A natural-based water-soluble carboxyalkylpolysaccharide is dissolved in water and recovered and heat-treated to form a carboxyalkyl polysaccharide which is water swellaable and water insoluble. The water-swellaable and water-insoluble carboxyalkyl polysaccharide having a preferred initial absorbency under load value is aged under at least about 60 percent relative humidity. In one aspect the aqueous mixture of water-soluble carboxyalkyl polysaccharide has a pH between about 4.0 and about 7.5. The natural-based material product having preferred absorbency under load and preferred aging characteristics retains at least about 50 percent of an initial Absorbency Under Load analytical testing value after aging.

**WO 01/87365 A3**





IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(88) Date of publication of the international search report:  
11 April 2002

**Declaration under Rule 4.17:**

— of inventorship (Rule 4.17(iv)) for US only

**Published:**

— with international search report

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/12761

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C08B11/20 C08B15/00 C08B37/00 A61L15/00 A61L15/28

According to international Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, CHEM ABS Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 11925 A (KIMBERLY-CLARK CORPORATION) 4 May 1995 (1995-05-04) cited in the application claims 39-49 ---	1-20
X	EP 0 538 904 A (KIMBERLY-CLARK CORPORATION) 28 April 1993 (1993-04-28)  claims ---	1,6-12, 15,17, 18,20
A	US 5 470 964 A (KIMBERLY-CLARK CORPORATION) 28 November 1995 (1995-11-28) claims ---	1
A	EP 0 566 118 A (KIMBERLY-CLARK CORPORATION) 20 October 1993 (1993-10-20) ---	
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\* & \* document member of the same patent family

Date of the actual completion of the international search

12 December 2001

Date of mailing of the international search report

21/12/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Mazet, J-F

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/12761

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 086 323 A (COURTAULDS LIMITED) 11 October 1967 (1967-10-11) ---	
A	US 3 731 686 A (CHATTERJEE) 8 May 1973 (1973-05-08) -----	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/12761

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9511925	A	04-05-1995	US 5550189 A	27-08-1996
			AU 687478 B2	26-02-1998
			AU 1084595 A	22-05-1995
			BR 9407917 A	26-11-1996
			CA 2130427 A1	30-04-1995
			CN 1139437 A	01-01-1997
			CZ 9601223 A3	16-10-1996
			EP 0739357 A1	30-10-1996
			HU 75504 A2	28-05-1997
			JP 9504331 T	28-04-1997
			PL 317098 A1	17-03-1997
			SK 49996 A3	05-03-1997
			WO 9511925 A1	04-05-1995
EP 538904	A	28-04-1993	AU 658455 B2	13-04-1995
			AU 2729192 A	29-04-1993
			BR 9204036 A	04-05-1993
			CA 2073292 A1	26-04-1993
			DE 69223587 D1	29-01-1998
			DE 69223587 T2	23-07-1998
			EP 0538904 A2	28-04-1993
			ES 2111032 T3	01-03-1998
			JP 5214001 A	24-08-1993
			KR 238386 B1	15-01-2000
			MX 9205548 A1	01-04-1993
			US 5247072 A	21-09-1993
			ZA 9207461 A	13-04-1993
US 5470964	A	28-11-1995	CA 2072918 A1	15-08-1993
EP 566118	A	20-10-1993	AU 3694993 A	21-10-1993
			AU 690844 B2	30-04-1998
			AU 5463896 A	01-08-1996
			CA 2076732 A1	18-10-1993
			DE 69313908 D1	23-10-1997
			DE 69313908 T2	26-03-1998
			EP 0566118 A1	20-10-1993
			ES 2107574 T3	01-12-1997
			JP 3221963 B2	22-10-2001
			JP 6025303 A	01-02-1994
			KR 244422 B1	01-02-2000
			MX 9301563 A1	01-10-1993
			US 5550189 A	27-08-1996
GB 1086323	A	11-10-1967	NONE	
US 3731686	A	08-05-1973	GB 1397154 A	11-06-1975
			BE 797833 A1	05-10-1973
			CA 969745 A1	24-06-1975
			CH 606517 A5	31-10-1978
			DE 2319309 A1	07-11-1974
			FR 2226977 A1	22-11-1974
			JP 1325273 C	16-07-1986
			JP 49130097 A	12-12-1974
			JP 56043427 B	12-10-1981
			NL 7305865 A	29-10-1974
			US 3858585 A	07-01-1975